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CHEMISTRY

OF THE

CARBON COMPOUNDS

OR

ORGANIC CHEMISTRY

BY

PROF. VICTOR von RICHTER,

UNIVERSITY OF BRESLAU.

AUTHORIZED TRANSLATION

BY

EDGAR F. SMITH,

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SECOND AMERICAN EDITION

FROM THE

SIXTH GERMAN EDITION.

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PREFACE TO SECOND EDITION.

The present American edition of *v. Richter's Organic Chemistry* will be found to differ very considerably, in its arrangement and size, from the first edition. The introduction contains new and valuable additions upon analysis, the determination of molecular weights, recent theories on chemical structure, electric conductivity, etc. The section devoted to the carbohydrates has been entirely rewritten, and presents the most recent views in regard to the constitution of this interesting group of compounds. The sections relating to the trimethylene, tetramethylene and pentamethylene series, the furfurane, pyrrol and thiophene derivatives, have been greatly enlarged, while the subsequent chapters, devoted to the discussion of the aromatic compounds, are quite exhaustive in their treatment of special and important groups. Such eminent authorities, as Profs. Ostwald, von Baeyer and Emil Fischer, have kindly supervised the author's presentation of the material drawn from their special fields of investigation.

The characteristic features of the first edition have been retained, so that the work will continue to be available as a text-book for general class purposes, useful and reliable as a guide in the preparation of organic compounds, and well arranged and satisfactory as a reference volume for the advanced student as well as for the practical chemist.

The translator would here express his sincere thanks to Prof. v. Richter, whose hearty co-operation has made it possible for him to issue this translation so soon after the appearance of the sixth German edition.

PREFACE

TO THE

FIRST AMERICAN EDITION.

The favorable reception of the American translation of Prof. von Richter's Inorganic Chemistry has led to this translation of the "Chemistry of the Compounds of Carbon," by the same author. In it will be found an unusually large amount of material, necessitated by the rapid advances in this department of chemical science. The portions of the work which suffice for an outline of the science are presented in large type, while in the smaller print is given equally important matter for the advanced student. Frequent supplementary references are made to the various journals containing original articles, in which details in methods and fuller descriptions of properties, etc., may be found. The volume thus arranged will answer not only as a text-book, and indeed as a reference volume, but also as a guide in carrying out work in the organic laboratory. To this end numerous methods are given for the preparation of the most important and the most characteristic derivatives of the different classes of bodies.

TABLE OF CONTENTS.

INTRODUCTION.

SPECIAL PART.

CLASS I.—FATTY BODIES OR METHANE DERIVATIVES.

Tetravalent Compounds.

Pentavalent Compounds.

Hexavalent Compounds.

Furfurane, Thiophene and Pyrrol Derivatives.

CLASS II. BENZENE DERIVATIVES.

(4) **With Condensed Benzene Nuclei.**

Derivatives of Nuclei containing Nitrogen.

(1) Derivatives of five-membered Nuclei.

(2) Derivatives of six-membered Nuclei.

ERRATA.

Page 78.—13th line from top, read *hexa-hydropseudo-cumene* for *mesitylene hexahydride.*

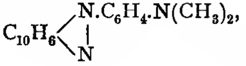
Page 313.—8th line from top, read *ethylene imine* identical with *piperazine* (p. 955).

Page 356.—1st line, read *pseudo-diketothiazole.*

Page 645.—21st line from bottom of page, read *disazo-derivatives* for *diazo-derivatives.*

Page 657.—14th line from bottom, read *a-methyl-phenyl-hydrazine,* instead of *a*-methylhydrazine.

Page 707.—8th line from bottom, read



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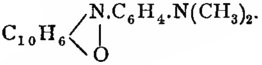


Page 788.—23d line from top, read *hydrogenized* for *hydrided.*

Page 874.—8th line from top, read *iodine* for *iodide.*

Page 912.—5th line from top, read *alicyclic* for *alicylic.*

A TEXT-BOOK

OF

ORGANIC CHEMISTRY.

INTRODUCTION.

The chemistry of the carbon compounds was formerly called *Organic Chemistry.* This designation originated in the time of Lavoisier (1743–1794), who announced the fundamental ideas of the nature of the chemical elements and compounds. He it was, too, who first recognized the true composition of the so-called *organic* substances occurring in the organism of plants and animals. He discovered that by their combustion, carbon dioxide and water were always formed, and showed that the component elements were generally carbon, hydrogen, and oxygen, to which sometimes—especially in animal substances—nitrogen was added. Lavoisier further gave utterance to the opinion that peculiarly constituted atomic groups, or radicals, were to be accepted as present in organic substances; while the mineral substances were regarded by him as the direct combinations of single elements.

In this way it was proved that the substances peculiar to the plant and animal kingdoms possess a composition different from that of mineral matter. As, however, it seemed impossible, for a long time, to prepare the former from the elements synthetically, the opinion prevailed that there existed an essential difference between the organic and inorganic substances; and this led to the distinction of the chemistry of the first as Organic Chemistry, and that of the second as Inorganic Chemistry. The prevalent opinion was, that the chemical elements in the living bodies were subject to other laws than those in the so-called inanimate nature, and that the organic substances were formed only in the organism by the intervention of a peculiar vital force, and that they could not possibly be prepared in an artificial way.

One fact sufficed to prove these rather restricted views to be unfounded. The first organic substance artificially prepared was urea (Wöhler, 1828). By this synthesis chiefly, to which others were soon added, the idea of a peculiar force necessary to the formation of organic compounds, was contradicted. However, even as late as 1840, Gerhardt clung to the view that chemical forces only exercise a destroying action, and with Berzelius, defined organic substances as those produced by vital force. Numerous additional syntheses soon showed that such opinions were no longer tenable. All further attempts to separate organic substances from the inorganic were futile. At present we know that these do not differ essentially from each other; that the peculiarities of organic compounds are dependent solely on the nature of their essential constituent, Carbon; and that all substances belonging to plants and animals, can be artificially prepared from the elements.

Organic Chemistry is, therefore, the *chemistry of the carbon compounds.* Its separation from general chemistry is demanded by practical considerations; it is occasioned by the very great number of carbon compounds.

We would here note the difference between the conceptions of *organic* and *organized* bodies. Different carbon compounds possess the power to assume in the living organisms an organized structure—to form cells. The causes and conditions of this power are as yet unknown to us. We know no more of them than of the cause of the union of molecules to form crystals, or of the atoms to form molecules.

Further, notice that organic chemistry does not occupy itself with the investigation of the chemical processes in vegetable and animal organisms. This is the office of *Physiological Chemistry.*

COMPOSITION OF CARBON COMPOUNDS.

ELEMENTARY ORGANIC ANALYSIS.

Most carbon compounds occurring in vegetables and animals consist of carbon, hydrogen, and oxygen. Many, also, contain nitrogen, and on this account these elements are termed *Organogens.* Sulphur and phosphorus are present in some naturally occurring substances. Almost all the elements, metalloids and metals, may be artificially introduced as constituents of carbon compounds in direct union with carbon. The number of known carbon compounds is exceedingly great, while the possible ones are almost without limit. The general procedure, therefore, of isolating the several compounds of a mixture, as is done in mineral chemistry in the separation of bases from acids, is impracticable. The mixtures occurring in vegetable and animal bodies, are only separated by special methods. The task of elementary organic analysis is to determine, qualitatively and quantitatively, the elements of a carbon compound after it has been obtained in a pure state and characterized by definite properties. The analysis is generally limited to the determinations of carbon, hydrogen, and nitrogen. Simple practical methods for the direct determination of oxygen do not exist. Its quantity is usually calculated by difference, after the other constituents have been found.

DETERMINATION OF CARBON AND HYDROGEN.

The presence of carbon in a substance is shown by its charring when ignited away from air. Ordinarily its quantity, as also that of the hydrogen, is ascertained by combustion. The substance is mixed in a glass tube with copper oxide and heated. Carbon burns to carbon dioxide, the hydrogen to water. In quantitative analysis, these products are collected in separate vessels, and the increase in weight of the latter determined. Carbon and hydrogen are always simultaneously determined in one operation. The details of the quantitative analysis are fully described in the text-books of analytical chemistry. It is only necessary here, therefore, to outline the methods employed. As a usual thing, the combustion is effected by the aid of copper oxide in a tube of hard glass, fifty to sixty centimetres long, and drawn into a point at one end (Fig. 1).

FIG. 1.

Dry, freshly ignited, granular copper oxide is first introduced into the tube (from *a* to *b*); then the mixture of the solid substance (about 0.2–0.3 gr.) with pulverized cupric oxide (*b* to *c*), and afterwards granular copper oxide (to *d*), upon which is placed a wad of asbestos. If the substance to be analyzed is a liquid, it is weighed out in a glass bulb drawn out to a point, and this placed in the combustion tube. When the latter has been filled, the open end is closed with a cork, carrying a straight or bent calcium chloride tube (Fig. 2).

This is filled with dried granulated chloride of calcium, which absorbs the aqueous vapor produced in the combustion tube, while the carbon dioxide passes on unchanged. To the calcium chloride tube is attached, by means of rubber tubing, a Liebig bulb (Fig. 3), containing potassium hydroxide (of sp. gr. 1.27); the potash bulb of Geissler is better. The carbon dioxide formed in the combustion is absorbed in this. To the potash bulb there is also attached a small tube; this is filled with stick potash. It serves to retain the slight quantity of aqueous vapor which might escape from the bulbs. Before the combustion takes place, the calcium chloride tube and the apparatus containing potassium hydroxide (also the small tube) are weighed separately. Their connection is then made, and the combustion tube placed in the furnace. The arrangement of the apparatus is illustrated in (Fig. 4).

FIG. 2.

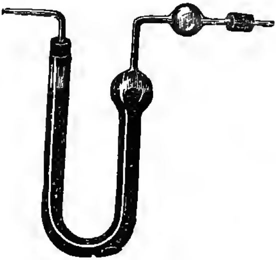
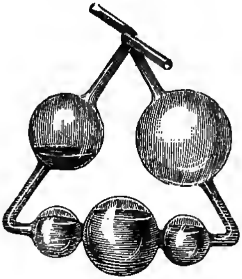
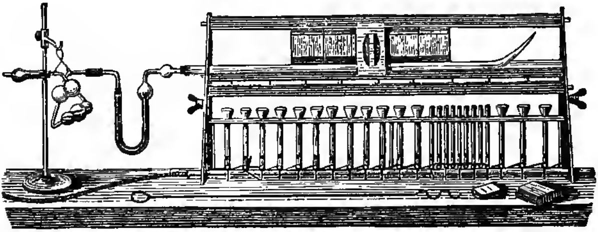


FIG. 3.



The front and back portions of the combustion tube are heated first. These parts contain only pure cupric oxide. Subsequently the middle portion, containing the substance, is gradually and partially heated. The heat should be so applied that the liberated carbon dioxide enters the potash bulbs in separate bubbles. When this no longer occurs the combustion is complete. The flames are then extinguished, the draw-out end of the tube is connected, by means of rubber tubing, with a drying apparatus; the point of the tube is broken off and air drawn through, to remove all aqueous

FIG. 4.



vapor and carbon dioxide from the combustion tube, and to bring them into their proper absorption vessels (the drying apparatus removes moisture and carbon dioxide from the aspirated air). When the substance is difficult to burn, it is advisable finally to conduct a stream of oxygen through the combustion tube, in order that all the carbon may be converted into carbon dioxide. After completing the operations just outlined, disconnect the apparatus and weigh the various pieces separately. The increase in weight of the calcium chloride tube represents the quantity of water produced; that of the potash bulbs, the amount of carbon dioxide. From these we can readily calculate the quantity of carbon and hydrogen in the substance analyzed.

Instead of mixing the substance with cupric oxide, it may be placed in a porcelain or platinum boat, then introduced into a tube open at both ends. The combustion in this case is carried out in a stream of air or oxygen—method of Glaser (Fig. 5).

A layer of granular copper oxide fills the tube from *d* to *e* (enclosed by two asbestos wads). This is ignited in a current of air, then allowed to cool. The end (*f*) is connected with the usual apparatus, previously weighed; the boat containing the substance (*c*) is introduced at the opposite end, and the latter joined either to an oxygen gasometer or some apparatus for purifying gases. The layer of cupric oxide is brought to a red heat, and the combustion executed in a slow current of air or oxygen. To avoid a diffusion of the gases backward in the tube, there is placed immediately behind the boat a wad (*b*) of asbestos or some copper; or a layer of mercury is introduced between the drying apparatus and the combustion tube. A second analysis may be commenced as soon as the first is ended.

FIG. 5.

In this last method, platinum black (mixed with asbestos) may be substituted for cupric oxide :—method of Kopfer. A much shorter and more simple combustion furnace may then be employed. The method is adapted to the combustion of compounds containing the halogens (*Zeitschrift für anal. Chemie*, 1878, 17, 1). Dudley has found that a platinum tube, having a layer of granular manganic oxide in the anterior part, is of great service when substances are placed in boats and exposed to combustion (*Ber.*, 21, 3172).

When nitrogen is present in the substances burned, oxides of it are sometimes produced, and these are absorbed in the calcium chloride tube and potash bulbs. To avoid this source of error, the oxides must be reduced to nitrogen. This may be accomplished by conducting the gases of the combustion over a layer of metallic copper filings, or a copper spiral, placed in the front portion of the combustion tube. The latter, in such cases, should be a little longer than usual. The copper is previously reduced in a current of hydrogen, then ignited, when it often includes hydrogen, which subsequently becomes water. To remedy this, the copper heated in a current of hydrogen is raised to a temperature of 200° in an air-bath, or better, in a current of carbon dioxide or in a vacuum. Its reduction by the vapors of formic acid or methyl alcohol is more advantageous; this may be done by pouring a small quantity of these liquids into a dry test tube and then suspending in them the roll of copper heated to redness; copper thus reduced is perfectly free from hydrogen. It is generally unnecessary to use a copper spiral when the combustions are executed in open tubes, because nitric oxide (NO) only is produced, and this passes through the caustic potash unabsorbed (*Ber.*, **22**, 3066, *Not.*).

In the presence of chlorine, bromine or iodine, halogen copper compounds (CuX) arise. These are somewhat volatile and pass over into the calcium chloride tube. The placing of a spiral of copper or silver foil in the front part of the tube will obviate this. When the organic compound contains sulphur a portion of the latter will be converted into sulphur dioxide, during the combustion with cupric oxide. This may be combined by introducing a layer of lead peroxide (*Zeitschrift f. anal. Chemie*, 17, 1). Or lead chromate may be substituted for the cupric oxide. This would convert the sulphur into non-volatile lead sulphate. In the combustion of organic salts of the alkalies or earths, a portion of the carbon dioxide is retained by the base. To prevent this and to expel the CO_2, the substance in the boat is mixed with some potassium bichromate or chromic oxide (*Berichte*, 13, 1641). When carbon alone is to be determined this can be effected, in many instances, in the wet way, by oxidation with chromic acid and sulphuric acid (*Messinger*, *Ber.*, **21**, 2910).

DETERMINATION OF NITROGEN.

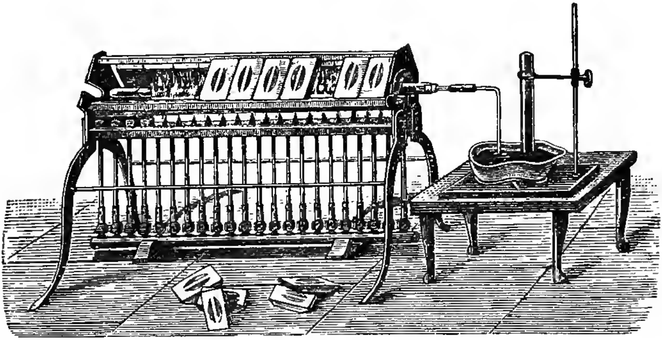
In many instances, the presence of nitrogen is disclosed by the odor of burnt feathers when heat is applied to the compounds under examination. Many nitrogenous substances yield ammonia when heated with alkalies (best with soda-lime). A simple and very delicate test for the detection of nitrogen is the following: Heat the substance under examination in a test tube with a small piece of sodium or potassium. When the substance is explosive, add dry soda. Cyanide of potash, accompanied by slight detonation, is the product. Treat the residue with water; to the filtrate add ferrous sulphate, containing a ferric salt, and a few drops of potassium hydroxide, then apply heat and add an excess of hydrochloric acid. An undissolved, blue-colored precipitate (Prussian blue), or a bluish-green coloration, indicates the presence of nitrogen in the substance examined.

Nitrogen is determined, quantitatively, either by volume, by burning the substance and collecting the liberated, free nitrogen, or as ammonia, by igniting the substance with soda-lime. The first method is applicable with all substances, while the second can only be employed with the amide and cyanide compounds, not with those containing the nitro- and the azo- groups.

1. **Method of Dumas.**—In a glass tube sealed at one end (length 70–80 cm.), place a layer (about 20 cm.) of dry, primary sodium carbonate or magnesite, then pure cupric oxide (6 cm.), afterwards the mixture of the substance with oxide, then again pure granular cupric oxide (20–30 cm.), and finally fill the tube with pure copper turnings (page 22) (about 20 cm.). In the open end of the tube is placed a rubber cork bearing a gas-delivery tube, which extends into a mercury bath.

The back part of the combustion tube, containing the carbonate, is heated first; this causes the liberated carbon dioxide to expel the air from all parts of the apparatus. We can be certain of this by placing a test tube filled with potassium hydroxide over the exit tube in the mercury trough. Complete absorption of the eliminated gas proves that air is no longer present. This done, a graduated cylinder filled with mercury is placed over the end of the exit tube and into the tube containing mercury is introduced, by means of a pipette, several cubic centimetres of concentrated potassium hydroxide. Proceed now with the combustion. First heat the metallic copper and the layer of cupric oxide in the anterior portion of the tube, and afterwards gradually approach the mixture. When the combustion is ended, again apply heat to another part of the sodium carbonate layer, to insure the removal of all the nitrogen from the tube and its entrance into the graduated tube. The potassium hydroxide absorbs all the disengaged carbon dioxide, and only pure nitrogen remains in the graduated vessel. The latter is then placed in a large cylinder of water, allowed to stand a short time until the temperature is equalized, when the volume of gas is read and the temperature of the surrounding air and the barometer

FIG. 6.



height noted. With these data, the weight (G) of the nitrogen volume, in grams, may be calculated from the formula—

$$G = \frac{V\,(h - w)}{760\,(1 + 0.00367\,t)} \times 0.0012562,$$

in which V represents the observed volume in cubic centimetres, h the barometric pressure, and w the tension of aqueous vapor at the temperature t. The number 0.0012562 is the weight, in grams, of 1 c. c. nitrogen at 0° C. and 760 mm. pressure.

Instead of reducing the observed gas volume V, from the observed barometric pressure and the temperature at the time of the experiment, to the normal pressure of 760 mm. and the temperature of 0° (as recommended in the preceding formula), the reduction may be more readily effected by comparing the observed volume of gas or vapor with the expansion of a normal gas-volume (100) measured at 760 mm. and 0°. For this purpose employ the equation $V_0 = V.\frac{100}{v}$, in which v represents the changed normal volume (100). The apparatus recommended by Kreusler (*Ber.*, 17, 30) and Winkler (*Ber.*, 18, 2534), or even the Lunge nitrometer will answer very well for this purpose.

The nitrogen determinations, as a general thing, are a little high in result, because it is almost impossible to expel the air from the combustion tube, and the metallic copper sometimes contains H (page 22). It is, therefore, well to remove the air from the tube by a mercury air-pump (*Zeitschrift f. analyt. Chemie*, 17, 409). Frankland conducts the combustion in a vacuum, and dispenses with the layer of metallic copper in the anterior portion of the tube. If any nitric oxide is formed it is collected together with the nitrogen, and is subsequently removed by absorption (*Ber.*, 22, 3065).

Instead of collecting the disengaged nitrogen in an ordinary graduated glass tube, peculiar "azotometers" may be employed. Of these the apparatus of Schiff (*Berichte*, 13, 886), Zulkowsky (*ibid.*, 1099), Groves (*ibid.*, 1341), and Ilenski (*ibid.*, 17, 1348), may be recommended. Consult the *Zeitschrift für analyt. Chemie*, 17, 409, and *Ber.*, 19, Ref. 710, for methods by which carbon, hydrogen, and nitrogen are determined simultaneously.

See Gehrenbeck (*Ber.*, 22, 1694) when a method is desired for the simultaneous estimation of nitrogen and hydrogen in cases where the carbon was determined in the wet way.

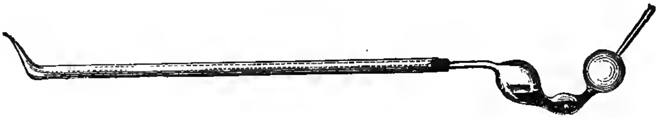
We can determine the nitrogen of nitro- and nitroso-compounds indirectly with a titrated solution of stannous chloride. The latter converts the groups NO_2 and NO into the amide group, with production of stannic chloride; the quantity of the latter is learned by the titration of the excess of stannous salt with an iodine solution. Method of Limpricht (*Berichte*, 11, 40).

2. **Method of Will and Varrentrap.**—When most nitrogenous organic compounds (nitro-derivatives excepted) are ignited with alkalies, all the nitrogen is eliminated in the form of ammonia gas. The so-called soda-lime is best adapted for this decomposition; it is prepared by adding 2 parts lime hydrate to the aqueous solution of pure sodium hydroxide (1 part), then evaporating the mixture and gently igniting it. Mix the weighed, finely pulverized substance with soda-lime (about 10 parts), place the mixture

in a combustion tube about 30 cm. in length, and fill in with soda-lime. In the open end of the tube there is placed a rubber cork bearing a bulb apparatus (Fig. 7), in which there is dilute hydrochloric acid. The anterior portion of the tube is first heated in the furnace, then that containing the mixture. To carry all the ammonia into the bulb, conduct air through the tube, after breaking off the point. The ammonium chloride in the hydrochloric acid is precipitated with platinic chloride, as ammonio-platinum chloride ($PtCl_4$. $2NH_4Cl$), the precipitate ignited, and the residual Pt weighed; 1 atom of Pt corresponds to 2 molecules of NH_3 or 2 atoms of nitrogen.

Generally, too little nitrogen is obtained by this method. A portion of the ammonia suffers decomposition. This is avoided by adding sugar to the mixture of substance and soda-lime, and by not heating the tube too intensely (*Zeitschrift*, 19, 91). It is also advisable to fill up the tube with soda-lime as far as is possible (*Zeit. für analyt. Chemie*, 22, 280). A more rapid volumetric method may be substituted for the gravimetric method in determining the ammonia. A definite volume of acid is placed in the bulb apparatus, and its excess after combustion ascertained by residual titration, employing fluoresceïn or methyl orange as indicator.

FIG. 7.



The method of Will and Varrentrap is made more widely applicable by adding reducing substances to the soda-lime. Goldberg uses a mixture of soda-lime (100 parts), stannous sulphide (100 parts), and sulphur (20 parts); this he considers especially advantageous in estimating the nitrogen of nitro- and azo-compounds (*Ber.*, 16, 2549). For nitrates, C. Arnold (*Ber.*, 18, 806) employs a mixture of soda-lime (2 parts), sodium hyposulphite (1 part), and sodium formate (1 part).

3. **Method of Kjeldahl.**—The substance is dissolved by heating it with concentrated sulphuric acid. Potassium permanganate (pulverized, or its solution in sulphuric acid) is then added until a distinct green color appears. This treatment decomposes the organic matter; its nitrogen is converted into ammonia. After the liquid has been diluted with water the ammonia is expelled from it by boiling with sodium hydroxide (*Zeit. f. a. Chem.*, 22, 366). This method is well adapted for the determination of the nitrogen of plants (compare *Ber.*, 18, Ref. 199).

When estimating the nitrogen of nitro- and cyanogen compounds it will be found decidedly advantageous to add sugar, and with nitrates, benzoic acid. The addition of potassium permanganate will be unnecessary. Pyridine and quinoline cannot be analyzed by this method (*Ber.*, 19, Ref. 367, 368).

DETERMINATION OF THE HALOGENS.

Substances containing chlorine and bromine yield, when burned, a flame having a green-tinged border. The following reaction is exceedingly delicate. A little cupric oxide is placed on a platinum wire, ignited in a flame until it appears colorless, when a little of the substance under examination is put on the cupric oxide and this heated in the non-luminous gas flame. The latter is colored an intense greenish-blue in the presence of chlorine or bromine. More decisive is to ignite the substance in a test tube with burnt lime, dissolve the mass in nitric acid, and then add silver nitrate.

The following *quantitative* methods for estimating halogens are in use:—

1. A hard glass tube, closed at one end, and about 30 cm. in length, is partly filled with calcium oxide, then the mixture of the substance with lime, followed by a layer of calcium oxide. The latter should be free of chlorine. Heat the tube in a combustion furnace; after cooling shake its contents into dilute nitric acid, filter, add silver nitrate and weigh the precipitated silver haloid.

The decomposition is easier, if we substitute for lime a mixture of lime with ¼ part sodium carbonate, or 1 part sodium carbonate, with 2 parts potassium nitrate, and in the case of substances volatilizing with difficulty, a platinum or porcelain crucible, heated over a gas lamp, may be used (*Ann.*, 195, 295 and 190, 40). With compounds containing iodine, iodic acid is apt to form; but after solution of the mass this may be reduced by sulphurous acid. The volumetric method of Volhard (*Ann.* 190, 1) for estimating halogens by means of ammonium sulphocyanide may be employed instead of the customary gravimetric course.

The same decomposition can also be effected by ignition with ferric oxide (*Berichte*, 10, 290).

2. **Method of Carius.**—The substance, weighed out in a small glass tube, is heated together with concentrated HNO_3 and silver nitrate to 150–300° C., in a sealed tube, and the quantity of the resulting silver haloid determined. The furnace of Babo (*Berichte*, 13, 1219) is especially adapted for the heating of tubes.

In some cases the substance may also be oxidized by the method proposed by P. Klason (p. 27).

3. In many instances, especially when the substances are soluble in water, the halogens may be separated by the action of sodium amalgam, and converted into salts, the quantity of which is determined in the filtered liquid.

DETERMINATION OF SULPHUR AND PHOSPHORUS.

The presence of sulphur is often shown by fusing the substance examined with potassium hydroxide; potassium sulphide results, and produces a black stain of silver sulphide on a clean piece of silver.

Heating the substance with metallic sodium is more accurate and always succeeds (even when sulphur is combined with oxygen): the aqueous filtrate is tested for sodium sulphide with sodium nitro-prusside.

In estimating sulphur and phosphorus ignite the weighed substance with a mixture of saltpetre and potassium carbonate; or, according to Carius, oxidize it by heating with nitric acid in a sealed tube (see *Ber.*, **20**, 2928). The resulting sulphuric and phosphoric acids are estimated by the usual methods.

Brügelmann employs a method not only applicable in the case of sulphur and phosphorus, but also adapted for the halogens. He burns the substances in an open combustion tube in a current of oxygen, conducting the products through a layer of pure granular lime (or soda-lime), which is placed in the same tube, and raised to a red heat. Later, the lime is dissolved in nitric acid, the halogens precipitated by silver nitrate, the sulphuric acid by barium chloride and the phosphoric acid (after removal of the excess of silver by HCl) by uranium acetate. Arsenic may be determined similarly (*Zeits. f. anal. Chemie*, **15**, 1 and 16, 1). Sauer recommends collecting the sulphur dioxide, arising in the combustion of the substance, in hydrochloric acid containing bromine (*Ibid.*, **12**, 178). To determine sulphur and the halogens by the method suggested by P. Klason (*Ber.*, **19**, 1910), the substance is oxidized in a current of oxygen charged with nitroso-vapors. The products of combustion are conducted over rolls of platinum foil. Consult Th. Poleck (*Zeit. f. a. Chem.*, **22**, 17) upon a method which is applicable for the estimation of the sulphur contained in coal gas.

Sulphur and phosphorus can often be estimated by the wet method. The oxidation is effected by means of potassium permanganate and caustic alkali, or with potassium bichromate and hydrochloric acid (Messinger, *Ber.*, **21**, 2914).

DETERMINATION OF THE MOLECULAR FORMULA.

The elementary analysis affords the percentage composition of the analyzed substance. There remains, however, the deduction of the atomic-molecular formula.

We arrive at the simplest ratio in the number of elementary atoms contained in a compound, by dividing the percentage numbers by the respective atomic weights of the elements. Thus, the analysis of lactic acid gave the following percentage composition:—

Carbon	40.0	per cent.	
Hydrogen	6.6	"	
Oxygen	53.4	"	(by difference.)
	100.0		

Dividing these numbers by the corresponding weights (C = 12, H = 1, O = 16), the following quotients are obtained:—

$$\frac{40.0}{12} = 3.3 \qquad \frac{6.6}{1} = 6.6 \qquad \frac{53.4}{16} = 3.3$$

Therefore, the ratio of the number of atoms of C, H and O, in the lactic acid, is as 1 : 2 : 1. The simplest atomic formula, then, would be CH_2O; however, it remains undetermined what multiple of this formula expresses the true composition. Indeed, we are acquainted with different substances having the empirical formula CH_2O, for example oxymethylene, CH_2O, acetic acid, $C_2H_4O_2$, lactic acid, $C_3H_6O_3$, grape sugar, $C_6H_{12}O_6$, etc. With compounds of complicated structure, the derivation of the simplest formula is, indeed, unreliable, because various formulas may be deduced from the percentage numbers by giving due regard to the possible sources of error in observation. The true molecular formula, therefore, can only be ascertained by some other means. Three courses of procedure are open to us. First, the study of the chemical reactions, and the derivatives of the substance under consideration; this is common to all cases. Second, the determination of the vapor density of volatile substances. Third, determining certain properties of the solutions of soluble substances.

(1) *Determination of the Molecular Weight by the Chemical Method.*

This is applicable to all substances. It is generally very complicated, and does not invariably lead to definite conclusions. It consists in preparing derivatives, analyzing them and comparing their formulas with the supposed formula of the original compound. The problem becomes simpler when the substance is either a base or an acid. Then it is only necessary to prepare a salt, determine the quantity of metal combined with the acid, or of the mineral acid in union with the base, and from this calculate the equivalent formula. A few examples will serve to illustrate this.

Prepare the silver salt of lactic acid (the silver salts are easily obtained pure, and generally crystallize without water) and determine the quantity of silver in it. We find 54.8 per cent. Ag. As the atomic weight of silver = 107.7, the amount of the other constituent combined with one atom of Ag in silver lactate, may be calculated from the proportion—

$$54.8 : (100 - 54.8) :: 107.7 : x$$
$$x = 89.0.$$

Granting that lactic acid is monobasic, that in the silver salt one atom of H is replaced by silver, it follows that the molecular weight of the free (lactic) acid must = 89 + 1 = 90. Consequently, the simplest empirical formula of the acid, $CH_2O = 30$, must be tripled. Hence, the molecular formula of the free acid is $C_3H_6O_3 = 90$:

$C_3 = 36$	40.0
$H_6 = 6$	6.7
$O_3 = 48$	53.3

When we are studying a base, the platinum double salt is usually prepared. The constitution of these double salts is analogous to that of ammonio-platinum chloride—$PtCl_4.2(NH_3HCl)$—the ammonia being replaced by the base. The quantity of Pt in the double salt is determined by ignition, and calculating the quantity of the constituent combined with one atom of Pt (198 parts). From the number found, subtract six atoms of Cl and two atoms of H, then divide by two; the result will be the equivalent or molecular weight of the base.

(2) *Determination of the Molecular Weight from the Vapor Density.*

This method is much simpler than the first. The results are perfectly reliable. It is, however, limited to only those substances which can be gasified and volatilized without suffering decomposition. The method is based upon the law of Avogadro, according to which equal volumes of all gases and vapors at like temperature and like pressure, contain an equal number of molecules (see v. Richter's Inorganic Chemistry). The molecular weights are, therefore, the same as the specific gravities. As the specific gravity is compared with $H = 1$, but the molecular weights with $H_2 = 2$, we ascertain the molecular weights by multiplying the specific gravity by two. Should the specific gravity be referred to air = 1, then the molecular weight is equal to the specific gravity multiplied by 28.86 (since air is 14.43 times heavier than hydrogen).

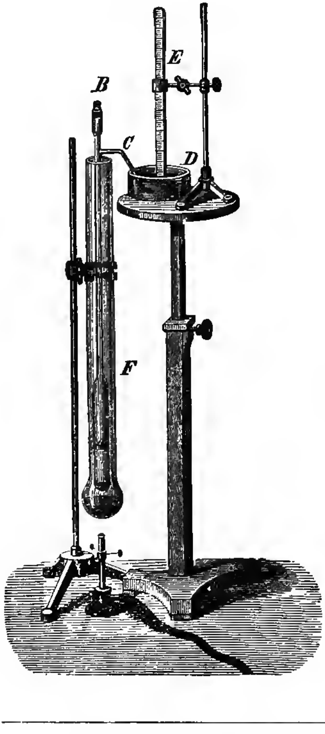
	Molecular Weight.		Specific Gravity.	
Air....................	—	—	14 43	1
Hydrogen	H_2	= 2	1	0.0693
Oxygen	O_2	= 31.92	15.96	1.1060
Chlorine.............	Cl_2	= 70.74	35.37	2.4550
Nitrogen	N_2	= 28	14	0.970
Hydrogen Chloride	HCl	= 36.37	18.18	1.260
Water.................	H_2O	= 18	9	0.622
Ammonia............	NH_3	= 17.96	8.98	0.589
Methane	CH_4	= 15.97	7.98	0 553
Ethane	C_2H_6	= 29.94	14.97	1.037
Pentane	C_5H_{12}	= 71.85	35.92	2.489
Ethylene.............	C_2H_4	= 27.94	13.97	0.964
Amylene.............	C_5H_{10}	= 69.85	34.92	2.430

The results arrived at by the chemical method, by transpositions, and those obtained by the physical method, by the vapor density—are always identical. Experience teaches this. If a deviation should occur, it is invariably in consequence of the substance suffering decomposition, or dissociation, in its conversion into vapor.

DETERMINATION OF THE VAPOR DENSITY.

Two essentially different principles underlie the methods employed in determining the vapor density. According to one, by weighing a vessel of known capacity filled with vapor, we ascertain the weight of the latter—method of Dumas. Or, in accordance with the other principle, a weighed quantity of substance is vaporized and the volume of the resulting vapor determined. In this case the vapor volume may be directly measured—methods of Gay-Lussac and A. W. Hofmann—or it may be calculated from the equivalent quantity of a liquid expelled by the vapor—displacement methods. The first three methods, of which a fuller description may be found in more extended text-books,* are seldom employed at present in laboratories, because the recently published method of V. Meyer, characterized by simplicity in execution, affords sufficiently accurate results for all ordinary purposes. Consult *Berichte*, 15,2777,21,2018, upon the applicability of the various methods.

Fig. 8.



Method of Victor Meyer.—Vapor density determination by *air displacement.*† According to this a weighed quantity of substance is vaporized in an enclosed space, when it displaces an equal volume of air, which is measured. Fig. 8 represents the apparatus constructed for this purpose. It consists of a narrow glass tube about 60 mm. long, to which is fused the cylindrical vessel, *A*, of 100 c.cm. capacity. The upper, somewhat enlarged opening, *B*, is closed with a caoutchouc stopper. There is also a short capillary gas-delivery tube, *C*, intended to conduct out the displaced air. It terminates in the water bath, *D*. The substance is weighed out in a small glass tube provided with a stopper, and vaporized in *A*. The escaping air is

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* Consult Handwörterbuch der Chemie, Ladenburg, Bd. 3, 244.

† *Ber.*, 11, 1867 and 2253.

collected in the eudiometer, *E*. The vapor-bath, used in heating, consists of a wide glass cylinder, *F*,* whose lower, somewhat enlarged end, is closed and filled with a liquid of known boiling point. The liquid employed is determined by the substance under examination; its boiling point must be above that of the latter. Some of the liquids in use are water (100°), xylene (about 140°), aniline (184°), ethyl benzoate (213°), amyl benzoate (261°), and diphenylamine (310°).

The air-baths, suggested by Lothar Meyer (*Ber.*, 16, 1091) can be used for heating purposes; they may be substituted for the vapor-baths.

The method of operation is as follows: First clean and dry the apparatus, *A B*, by drawing air through it by means of a long, thin, glass tube, and, for safety, cover the bottom of *A* with ignited asbestos, or thin platinum spirals. Next place it in the heating cylinder, *F*, containing about 200 c.cm. of the heating liquid, close *B* and dip the end of *C* into the water-bath, *D*. With a lamp bring the contents of *F* to boiling, and wholly encircle *A* with vapor, which condenses somewhat higher and flows regularly back. The air in *A* is thus heated, expands, and in part escapes from the side delivery tube through the water-bath. The non-evolution of air bubbles indicates a *constant* temperature in *A B*, which is now prepared to receive the substance. The cork at *B* is rapidly removed, and the substance (0.05–0.1 gr.) weighed out in a small glass vessel, permitted to drop into *A*, the opening is again closed, and the end of the delivery tube, *C*, placed under the graduated tube filled with water. An improved method for the introduction of the substance is described below. When the substance vaporizes it displaces an equal volume of air which collects in the graduated tube. The quantity of material taken for each determination is always small, because it is desirable that the volume of its vapor should not exceed 1/3 of the volume of *A*. As soon as bubbles are no longer emitted, the determination is finished. The graduated tube is placed to one side, the cork at *B* eased, to admit air and thus avoid the entrance of water when the apparatus cools. The volume of vapor formed is represented in the eudiometer by an equal volume of air, reduced to the temperature of the water-bath and given air pressure. Read off its volume and note the temperature and barometric pressure.

The calculation of the vapor density, S, from the volume of gas found and the quantity of substance employed is simple. It equals the weight of the vapor, P (afforded by the weight of the sub-

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* See *Ber.*, 19, 1862, for another form of vapor mantle.

stance employed), divided by the weight of an equal volume of air, P′—

$$S = \frac{P}{P'}.$$

1 c. cm. air at 0° and 760 mm. pressure weighs 0.001293 gram. The air volume found at the observed temperature is under the pressure H — w, in which H indicates the barometric pressure and w the tension of the aqueous vapor at temperature t. The weight then would be—

$$P' = 0.001293 . V . \frac{1}{1 + 0.00367\,t} . \frac{H - w^{*}}{760}.$$

Consequently, the vapor density sought is—

$$S = \frac{P\,(1 + 0.00367\,t.)\,760\,\dagger}{0.001293 .\ V . H - w}.$$

V. Meyer's method yields results that are perfectly satisfactory *practically*, although not without some slight error in principle. However, they answer, because in deducing the molecular weight from the vapor density, relatively large numbers are considered and the little differences discarded. A greater inaccuracy may arise in the method in filling in the substances as described, because air is apt to enter the vessel. L. Meyer (*Ber.*, 13, 991), Piccard (*ibid.*, 13, 1080), Mahlmann (*ibid.*, 18, 1624), and V. Meyer and Bilz (*ibid.*, 21, 688) have suggested different devices to avoid this source of error. To test the decomposability of the substance at the temperature of the experiment, heat a small portion of it in a glass bulb provided with a long point (see *Berichte*, 14, 1466)..

Substances boiling above 300° are heated in a lead-bath (*Berichte*, 11, 2255). Porcelain vessels are used when the temperature required is so high as to melt glass, and the heating is conducted in gas-ovens (*Berichte*, 12, 1112). Where air affects the substances in vapor form, the apparatus is filled with pure nitrogen. (Compare *Ber.*, 18, 2809; 21, 688). When the substances under investigation attack the porcelain, tubes of platinum are substituted for the latter. These are enclosed in glazed porcelain tubes, and heated in furnaces (*Ber.*, 12, 2204; *Zeit. phys. Chem.*, 1, 146; *Ber.*, 21, 688). This form of apparatus allows of the simultaneous determination of temperature. The air or nitrogen which may be in them can be displaced by carbon dioxide or hydrochloric acid gas (*Ber.*, 15, 141. *Zeit. phys. Chem.*, 1, 153).

For modifications in methods of determining the density of gases, consult V. Meyer, *Berichte*, 15, 137, 1161 and 771; Langer and V. Meyer, *Pyrotechnische Untersuchungen*, 1885; Crafts, *Berichte*, 13, 851, 14, 356, and 16, 457. For air-baths and regulators, see L. Meyer, *Berichte*, 16, 1087; 17, 478; 18, 2838.

Modifications of the displacement method, adapted for work under reduced pressure, have been proposed by La Coste (*Ber.*, 18, 2122), Schall (*Ber.*, 20, 1827 and 2127; 21, 100), Malfatti (*Zeit. phys. Chem.*, 1, 159), and Eyckmann (*Ber.*, 22, 2754). For the method of Nilson and Petterson, see *Ber.*, 17, 987 and 19, Ref. 88; also *Jour. pr. Chem.*, 33, 1. See *Ber.*, 21, 2767, for the method of Bilz.

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* It is simpler to make the reduction to 760 mm. and 0° by comparison with a normal volume (p. 24).

† The calculation of the molecular weight can be made directly and more readily by using the equation given on p. 34.

(3) *Determination of the Molecular Weight of Substances when in Solution.*

1. **By means of Osmotic Pressure.**—Recently Van't Hoff has developed an exceedingly important theory in regard to solutions.* According to this new idea chemical substances, when in dilute solution, exhibit a deportment similar to that observed when in a gaseous or vapor-form; therefore, the laws applicable to gases (Boyle, Gay-Lussac and Avogadro) possess the same value for solutions. We know that the gas-particles exert pressure, and it is also true that the particles of compounds, when dissolved, exert a pressure, which is directly expressed or shown by the osmotic phenomena, and hence it is termed *osmotic pressure.* This pressure is equal to that which would be exerted by an equal amount of the substance, if it were converted into gas, and occupied the same volume, at the same temperature, as the solution. Solutions containing molecular quantities of different substances exert the same osmotic pressure. It is, therefore, possible, as in the case of gas-pressure, to directly deduce the molecular weight of the substances in solution from this osmotic pressure. The methods thus far employed for the determination of this pressure have been too complicated and time-consuming to permit of their application in practical work. The determination of the vapor pressure, or the freezing point of solutions is more suitable; these are intimately related to osmotic pressure (p. 35).

Pfeffer determines osmotic pressure by means of artificial cells, having semi-permeable walls. These are produced by saturating porous earthenware cells with solutions of copper sulphate, and potassium ferrocyanide. A sheet of copper ferrocyanide is formed in the wall of the cell, through which water can circulate, but not sugar or other substances which may be held in solution. The pressure exerted on the membranous cell, by the dissolved substances, is measured by the osmotic elevation, or by a manometer. If suitably modified this method promises to be of wide applicability (Ladenburg, *Ber.*, 22, 1225).

The *plasmolytic method* of de Vries (*Zeit. phys. Chem.*, 2, 415), employed in determining osmotic pressure, is based upon the use of living plant cells; the protoplasma of the latter is clothed with a thin pellicle (the protoblast), which is semi-permeable (see above). When such cells are introduced into aqueous solutions of definite concentration their membranes contract, if the external osmotic pressure exceeds that of the cell-contents (*Zeit. phys. Chem.*, 2, 415).

To calculate the molecular weight, make use of the general formula for gases: $pv = RT$, in which R represent a constant, and T the absolute temperature, caculated from — 273° forward.

If this equation is also to include the law of Avogadro (that the molecular weights of gases or dissolved substances occupy the same volume at like temperature and pressure), then molecular quantities of the substances must always be

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* Van't Hoff, *Zeit. phys. Chem.*, 1, 481; 3, 198. "Ein elementare Darstellung der Theorie der Lösungen," see Ostwald's "Grundriss der allgemeinen Chemie," 1889.

taken into consideration. The constant equals 84500 for gram molecular weights (2 grams hydrogen, or 31.92 grams oxygen) at the temperature 0° (or 273°), and the pressure (gas or osmotic pressure) of 76 cm. of mercury.

$$p \cdot v = 84500 \cdot T^*.$$

v represents the volume corresponding to the gram molecular weight $(v = \frac{M}{a}$, in which a is the weight in grams of 1 c.cm. of the gas, or dissolved substance, contained in 1 c.cm. of the solution). Substituting figures the formula would read: $p \cdot 13.59 \times \frac{M}{a} = 84500\,(273 + t)$, with the four variables p, M, a and t. If three of these be given the fourth can be calculated. Consequently, the molecular weight *M* is found from the formula:—

$$M = \frac{a \cdot 84500\,(273 + t)}{p \cdot 13.59} = \frac{a \cdot 6218\,(273 + t)}{p}.$$

2. **From the Lowering of the Vapor Pressure.**—The lowering of the vapor pressure of solutions is closely allied to osmotic pressure. It is a known fact that solutions at the same temperature have a lower vapor pressure (f′) than the pure solvent (f), and consequently boil at a more elevated temperature than the latter. The lowering in pressure (f — f′) is in proportion to the quantity of the substance dissolved (Wüllner). This harmonizes with the equation $\frac{f - f'}{f} = k.\,g$, in which k represents the "relative lowering of the vapor pressure" $\left(\frac{f - f'}{f}\right)$ for 1 per cent. solutions, and *g* their percentage content.

If the lowering be referred not to equal quantities, but rather to molecular quantities of the substances dissolved, it will be discovered that equi-molecular solutions (those containing molecular quantities of the different substances in equal amounts in the same solvent) show equal lowering—the molecular vapor pressure lowering is constant:—

$$M \cdot \frac{f - f'}{f} = C.$$

Again, on comparing the relative lowering of vapor pressure in different solvents, it will be found also that they are equal, if equal amounts of the substances are dissolved in molecular quantities of the solvent. In its broadest sense the law would read: The lowering of vapor-pressure is to the vapor-pressure of the solvent (f) as the number of molecules of the dissolved body (n) is to the total number of molecules (n + N):—

$$\frac{f - f'}{f} = \frac{n}{n + N}.$$

Substituting the quotients $\frac{g}{m}$ and $\frac{G}{M}$ (g and G represent the weight quantities of the substance and the solvent; m and M are their molecular weights), for n and N, it will be easy to calculate the molecular weights.

F. M. Raoult (1887) developed these rules empirically. Soon thereafter van't

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* $R = \frac{p\,v}{T}$; $p = 1033 = 76 \times 13.59$ (sp. gr. of mercury); $v = 22330 = 31.92/0.001430$ (wt. of 1 c.cm. of oxygen). $R = \frac{1033 \times 22320}{273}$.

Hoff (*Zeit. phys. Chem.*, 3, 115), deduced them theoretically from the osmotic pressure. They are only of value for non-volatile (as compared with the solvent) substances, or such as volatilize with difficulty. The same abnormalities observed with osmotic pressure and depression in the freezing point also appear here.

The methods for the determination of vapor-pressure are yet too little known and primitive in their nature to be applied in the practical determination of molecular weights (*Ber.*, **22**, 1084). It is easier to determine the rise in the boiling points; this is also more reliable (Beckmann, *Zeit. phys. Chem.*, 4, 5).

3. **From the Depression of the Freezing Point.**—The molecular weights of dissolved substances are more accurately and readily deduced from the depression of the freezing points of their solutions. Blagden in 1788, and Rüdorff in 1861, found that the depression of the freezing points of crystallizable solvents, or substances (as water, benzene and glacial acetic acid) is proportional to the quantity of substance dissolved by them. The later researches of Coppet (1871), and especially those of Raoult (1882), have established the fact that when molecular quantities of different substances are dissolved in the same amount of a solvent they show the same depression in their freezing points (Law of Raoult). If t represents the depression produced by p grams of substance in 100 grams of the solvent, the co efficient of depression $\frac{t}{p}$ will be the depression for 1 gram of substance in 100 grams of the solution.*

The *molecular depression* is the product obtained by multiplying the depression co-efficient and the molecular weight of the dissolved substances. This is a constant for all substances having the same solvent:—

$$M \cdot \frac{t}{p} = C.$$

Raoult's experiments show the constant to have the following values: for benzene 4.9; for glacial acetic acid 39; for water 19. When the constant is known the molecular weight is calculated as follows:—

$$M = C\,\frac{p}{t}.$$

A comparison of the constants found for different solvents will disclose the fact that they bear the same ratio to each other as the molecular weights—that consequently the quotient obtained from the molecular depressions and molecular weights is a constant value (about 0.62). It means, expressed differently, that the molecule of any one substance dissolved in 100 molecules of a liquid lowers the point of solidification very nearly 0.62.

Guldberg (1870) and van't Hoff (1886), have since made a theoretical deduction of these laws from the lowering of the vapor pressure, and from the osmotic

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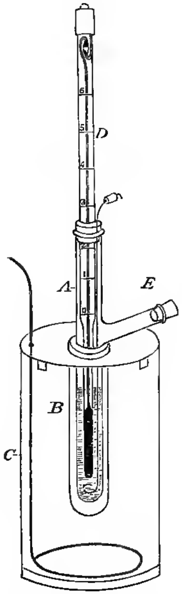
* Raoult (*Zeit. phys. Chem.*, **2**, 353). Arrhenius expresses the content of solutions by the weight in grams of the substances contained in 100 c.c. of the solution.

pressure. The constant *C* is obtained, for the various solvents, from the formula $0,02 \frac{T^2}{W}$. Here T indicates the temperature of solidification of the solvent calculated from the absolute zero-point forward. W is its latent heat of fusion. In this way van't Hoff calculated the constants for benzene (53), acetic acid (38.8), and water 18.9 (see above).

The laws just described possess a direct value for indifferent substances, having but slight chemical activity. Salts, strong acids and bases (all electrolytes) constitute the exceptions. The depressions in freezing point are greater for these than their calculated values (they also have greater osmotic pressure, and greater lowering of the vapor pressure). The electrolytic dissociation theory of Arrhenius * would account for this by the assumption that the electrolytes have separated into their free ions. However even the indifferent bodies exhibit many abnormalities—generally the very opposite of the ordinary. These seem to be due to the fact that the substances held in solution had not completely broken up into their individual molecules. The most accurate results are obtained by operating with very dilute solutions, and by employing glacial acetic acid as solvent. This dissociates solids most readily.

FIG. 9.



DETERMINATION OF THE DEPRESSION OF THE FREEZING POINT.

A weighed quantity of the solvent, is placed in a wide test-tube of hard glass, and its freezing point determined. In the mouth of the tube is a large cork through which a thermometer and a stirring rod pass. A weighed quantity of substance is now added to the solvent, and dissolved in it. The freezing point is again determined (Hollemann, *Ber.*, 21, 860).

Various forms of apparatus suitable for the above purpose, and methods of working have been proposed by Auwers, † Hentschel, ‡ Beckmann, § Eykmann, ‖ and Klobukow. ¶

Beckmann's Method.—A hard glass tube *A*, 2–3 cm., in width, with a side projection E (Fig. 9), is filled with 15–20 grams of the solvent (weighed out accurately in centigrams), and closed with a cork, in which are placed an accurate thermometer (Walferdin), and a stout platinum wire serving as a stirring rod. The lower part of the tube is attached by means of a cork to a somewhat larger, wider tube. The latter serves as an air-jacket. The entire apparatus projects into a beaker glass filled with a freezing mixture.

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* *Zeit. phys. Chem.*, 1, 631; 1, 577; 2, 491.

† *Ber.*, 21, 711; ‡ *Zeit. phys. Chem.*, 2, 307; § *Ibid.*, 2, 638; ‖ 2, 966; ¶ *Ibid.*, 4, 66.

Cold water will answer for glacial acetic acid (congealing at 16°), and ice-water for benzene (about 5°). First determine the congealing point of the solvent by cooling it 1–2° below its freezing point, and then by agitation with the platinum rod (after addition of platinum clippings), induce the formation of crystals. During this operation the thermometer rises, and when the mercury is stationary it indicates the freezing point of the solvent. Allow the mass to melt, and introduce an accurately weighed amount of substance through E. When this has dissolved the freezing point is re-determined as before.

Eykmann (*Zeit. phys. Chem.*, 2, 966) has designed a method by which it is possible to use smaller amounts of solution (6–8 grams) and substance. This is done by using phenol (m. p. about 38°), as the solvent. Its molecular depression has been theoretically deduced; it is about 76 (see above).

Paterno's investigations show, contrary to earlier observations, that the carbon derivatives mostly yield normal results; the exceptions being the alcohols, phenols, acids and oximes.*

Naphthalene may also be used for determinations of this kind. Van't Hoff gives its depression constant as equal to about 70 (*Ber.*, **22**, 2501; and Eykmann, *Ber.*, **23**, Ref. 1).

CHEMICAL STRUCTURE OF THE CARBON COMPOUNDS.

The molecular weight of a given substance and the absolute number of atoms contained in the latter, are ascertained by elementary analysis, and the study of the chemical transpositions, or by the determination of the vapor density. The problem of establishing the chemical formula of a compound would soon be solved, did not experience show that very often entirely different substances are possessed of the same molecular composition. *Isomerides* (from ἰσομερής, consisting of equal parts), is the name given these. In a more extended sense, isomerism includes all bodies of like percentage composition. When the isomerism depends upon a difference in molecular weight (p. 28), it is termed *polymerism;* a special case of the latter is the allotropy of the elements (see Richter's Inorganic Chemistry).

Real isomerism, *i. e.*, the phenomenon of bodies of like composition and like number of atoms, being different, is interpreted only by granting a different grouping or arrangement of the atoms in the molecule. That this, indeed, occurs, follows from the investigation of chemical reactions, as it is easy to split off from isomeric bodies entirely different atomic groups and atoms, or even to replace them by others. Hence, the atoms in such compounds are differently distributed or linked to one another. To investigate this different chemical union of the atoms, the *chemical constitution* of compounds—as an expression for their entire chemical deportment—is the task presented us. Since, however, the nature of chemical affinity and the manner of the union of atoms to mole-

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* *Ber.*, **22**, 1431, and *Zeit. phys. Chem.*, **5**, 94.

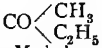
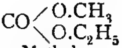
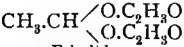
cules are absolutely unknown to us, the expression of chemical constitution can only be hypothetical—a mere formulation of the actually known regularities in the chemical transpositions of compounds.

The various attempts to formulate the chemical constitution of compounds belong to the history of chemistry (p. 47). At present, the problem, especially in its relation to the derivatives of carbon, is largely solved by the doctrine or theory of chemical structure. This is based upon the ideas of differences in valence in the elementary atoms, and upon their capability of combining by single affinity units (see Richter's Inorganic Chemistry).

Although the number of cases of isomerism is but limited in inorganic chemistry, and there being consequently but little importance attached to the presentation of structural formulas, the phenomena of this kind are exceedingly abundant with the carbon compounds, so that constitutional or structural formulas, representing the entire chemical deportment, are absolutely necessary. Frequently, very complicated relations occur, yet the structure of all investigated carbon derivatives may be deduced from the following principles:—

1. The carbon atoms, in their hydrogen combinations, are constantly quadrivalent. The position of carbon in the periodic system gives expression to this fact. The only derivative in which carbon apparently figures as a bivalent element is carbon monoxide, CO (see below).

2. The four affinity units of carbon are, as generally represented, equal and similar, *i. e.*, no differences can be discovered in them when they form compounds. If these four affinities be attached to different elements or groups, the order of their combination is entirely immaterial. The compounds—

CH_3Cl	$CH_3.NH_2$	$CH_3.COOH$	CH_3CH_3
Methyl Chloride.	Methyl Amine.	Acetic Acid.	Di-methyl.
CH_2Cl_2	 $CO\begin{cases}CH_3\\C_2H_5\end{cases}$	 $CO\begin{cases}O.CH_3\\O.C_2H_5\end{cases}$	 $CH_3.CH\begin{cases}O.C_2H_3O\\O.C_2H_3O\end{cases}$
Methyl Dichloride.	Methyl-ethyl Acetone.	Methyl-ethyl Carbonate.	Ethylidene Aceto-propionate.

are known in but one modification each; their isomerides have never been prepared.

3. The carbon atoms can unite in a chain-like series, by combining with each other by one or more units. This they can do, also, with other elementary atoms.

These principles express the relations really known at present All investigated compounds prove carbon to be quadrivalent. Carbon monoxide, CO, is not a contradiction, as valence is a relative function of the atoms (compare Richter's Inorganic Chemistry), and its existence is affected in the same way by the nature of oxygen, as by carbon; we can, with equal correctness, represent O in CO as quadrivalent and C as bivalent. Because CO does exist, it in no manner follows that carbon can figure as a dyad in the hydrogen derivatives. Repeated efforts to prepare compounds containing bivalent carbon were unsuccessful (page 42).

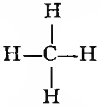
The equi-valence of the four carbon affinities, in the sense above illustrated, has likewise been positively confirmed. By the early type or substitution theory, it appeared possible that compounds like

$$CH_3Cl \text{ and } CClH_3 \text{ or } CH_3NH_2 \text{ and } NH_2CH_3, \text{ etc.,}$$

were isomeric. All experiments instituted proved that the succession of substitution or the replacement of the substituting atoms again were without effect; identical bodies resulted in all analogous cases.

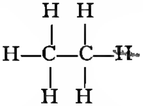
It may be added, in regard to the capability of union of the carbon atoms with each other and with other elements, that all the imaginable combinations are really not possible. Certain groupings can in no way be realized, and the union of two atoms is very often influenced by the atoms present with them in the molecule. The related phenomena, which are of such great interest as regards the constitution, will be developed later, in special cases.

The different manner, in the linking of the carbon atoms, shows itself most plainly in their hydrogen compounds—in the so-called hydrocarbons. By removing one atom of hydrogen from the simplest hydrocarbon, methane, CH_4, the remaining univalent group, CH_3, can combine with another, yielding $CH_3—CH_3$, or C_2H_6, ethane or dimethyl. Here, again, a hydrogen atom may be replaced by the group CH_3, resulting in the compound $CH_3—CH_2—CH_3$ propane. The structure of these derivatives may be more clearly represented graphically:—



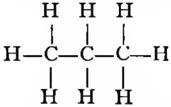
$$\begin{array}{ccc} & H & \\ & | & \\ H— & C & —H \\ & | & \\ & H & \end{array}$$

CH_4



$$\begin{array}{cccc} & H & H & \\ & | & | & \\ H— & C— & C— & H \\ & | & | & \\ & H & H & \end{array}$$

C_2H_6



$$\begin{array}{ccccc} & H & H & H & \\ & | & | & | & \\ H— & C— & C— & C— & H \\ & | & | & | & \\ & H & H & H & \end{array}$$

etc.

C_3H_8

By continuing this chain-like union of the carbon atoms, there arises an entire series of hydrocarbons:—

$$\underset{C_4\,H_{10}}{CH_3 — CH_2 — CH_2 — CH_3} \qquad \underset{C_5\,H_{12}}{CH_3 — CH_2 — CH_2 — CH_2 — CH_3}, \text{ etc.}$$

having the common formula $C_n\,H_{2n+2}$, in which each member differs from the one immediately preceding and the one following, by CH_2.

The compounds constituting such a series are said to be *homologous*. In addition to the hydrocarbons forming such a series, many others exist, *e. g.*, the monohydric alcohols and monobasic acids:—

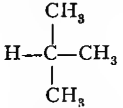
CH_4	CH_4O	CH_2O_2
C_2H_6	C_2H_6O	$C_2H_4\,O_2$
C_3H_8	C_3H_8O	$C_3H_6\,O_2$
C_4H_{10}	$C_4H_{10}O$	$C_4H_8\,O_2$
C_5H_{12}	$C_5H_{12}O$	$C_5H_{10}O_2$

The compounds belonging to such an homologous series, because of their similarity in chemical structure, exhibit great analogy in their entire chemical character.

The manner of union just considered, that of a simple, open chain, is designated *normal structure.* In this we distinguish intermediate and terminal carbon atoms; the first are connected with two other carbon atoms and have two valence units which may be saturated by two hydrogen atoms (or other elements). The terminal carbon atoms of the chain are combined with three hydrogen atoms. Usually, the normal structure may be expressed by the following formulas:—

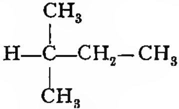
$$CH_3 - (CH_3)_n - CH_3 \text{ or } (CH_2)_n\begin{matrix}\diagup CH_3\\ \diagdown CH_3\end{matrix}$$

Carbon atoms can unite with even three or four other carbon atoms, then *tertiary* or *quaternary* union or structure arises:



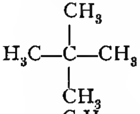
$$\begin{matrix} & CH_3 & \\ & | & \\ H— & C & —CH_3 \\ & | & \\ & CH_3 & \end{matrix}$$

C_4H_{10}
Tertiary
Butane.



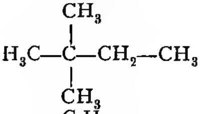
$$\begin{matrix} & CH_3 & \\ & | & \\ H— & C & —CH_2—CH_3 \\ & | & \\ & CH_3 & \end{matrix}$$

C_5H_{12}
Tertiary
Pentane.



$$\begin{matrix} & CH_3 & \\ & | & \\ H_3C— & C & —CH_3 \\ & | & \\ & CH_3 & \end{matrix}$$

C_5H_{12}
Quaternary
Pentane.



$$\begin{matrix} & CH_3 & \\ & | & \\ H_3C— & C & —CH_2—CH_3 \\ & | & \\ & CH_3 & \end{matrix}$$

C_6H_{14}
Quaternary
Hexane.

This varying union of the carbon atoms explains the numberless isomerides possible for the higher series. This will be especially observed in case of the hydrocarbons.

In all the structural cases introduced here, the two carbon atoms are in simple combination with each other. The number of valence units (hydrogen atoms) with which the carbon nuclei consisting of *n* atoms can directly combine equals 2n + 2 (p. 39). This cannot be exceeded without the consequent destruction of the carbon nucleus. Therefore, compounds constituted according to the general formula C_nX_{2n+2} (in which X represents the valences directly joined to C), are termed *saturated* compounds or paraffins.

Besides the hydrocarbons C_nH_{2n+2}, there exists another homologous series (p. 39) of the form C_nH_{2n}:—

C_2H_4	Ethylene.
C_3H_6	Propylene.
C_4H_8	Butylene.
C_5H_{10}	Amylene, etc., etc.

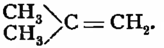
Their existence is accounted for by assuming that in them two carbon atoms are united by two valences—a *double* or *bivalent* union. The following structural formulas indicate this:—

$CH_2 = CH_2$ Ethylene. $CH_3 - CH = CH_2$ Propylene.

For the formula C_4H_8, three structures are possible:—

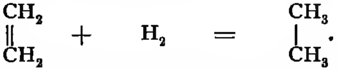
$CH_3 - CH_2 - CH = CH_2$ $CH_3 - CH = CH - CH_3$

and



$$\begin{matrix} CH_3 \diagdown \\ CH_3 \diagup \end{matrix} C = CH_2.$$

As only a simple union is required for the linking of the carbon atoms, such compounds as the last are yet capable of saturating two valence units; they are, therefore termed *unsaturated* compounds. By the addition of two hydrogen atoms, they pass into C_nH_{2n+2}. The double changes to single union:—



$$\begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix} + H_2 = \begin{matrix} CH_3 \\ | \\ CH_3 \end{matrix}.$$

The acceptance of this double union of the carbon atoms in no manner indicates (as sometimes erroneously supposed) a close, stronger combination. It has long been known, that the unsaturated compounds could be much more readily broken up than the saturated; and that they possess, too, a greater specific volume; hence, the double union is *less intimate* than the simple. (Compare 1st Ed. of this book, p. 40.) The use of the double lines represents the fact that only two directly combined carbon atoms are capable of saturation (p. 39).

That the unsaturated compounds do possess a greater heat of combustion is an argument in favor of the view that the union of the carbon atoms is less intimate. A. Baeyer (*Ber.*, 18, 2277) has published an experimental proof of this deportment.

A third series of hydrocarbons arises when a triple union of two carbon atoms occurs. Their composition corresponds to the common formula C_nH_{2n-2}:—

C_2H_2	Acetylene.
C_3H_4	Allylene.
C_4H_6	Crotonylene, etc.

Their structural formulas are—

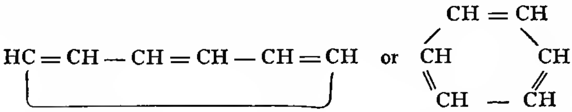
$CH \equiv CH$ $CH_3 - C \equiv CH$ $CH_3 - CH_2 - C \equiv CH.$

We can view these as unsaturated hydrocarbons of the second degree. They are capable of combining directly with two and four valences, passing into the compounds C_nH_{2n} or C_nH_{2n+2}.

Compounds containing a like number of carbon atoms, with a gradually decreasing number of hydrogen atoms, are designated *isologous* compounds. The following are examples:—

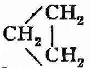
C_2H_6	Ethane.	C_3H_8	Propane.	C_3H_8O	Propyl alcohol.
C_2H_4	Ethylene.	C_3H_6	Propylene.	C_3H_8O	Allyl alcohol.
C_2H_2	Acetylene.	C_3H_4	Allylene.	C_3H_4O	Propargylic alcohol.

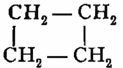
Finally, there is a large series of carbon compounds bearing the name aromatic. They all originate from a nucleus composed of six carbon atoms. Benzene, C_6H_6, represents their simplest combination. The simplest structure of this nucleus is probably one in which the six carbon atoms form a closed ring, with alternating single and double union, as represented by the following:—

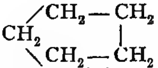


The innumerable aromatic or benzene compounds resulting from the replacement of H in benzene by other atoms or groups, constitute a distinct class.

The ring-shaped compounds trimethylene, C_3H_6, tetramethylene, C_4H_8, and pentamethylene, C_5H_{10}, recently described, are forerunners of the stable, closed benzene ring:—


Trimethylene.


Tetramethylene.


Pentamethylene.

A series of compounds is likewise derived by the replacement of hydrogen in the preceding hydrocarbons.

Formerly, another view prevailed relative to the unsaturated carbon compounds. It was assumed that bivalent carbon atoms could occur in the hydrogen compounds, just as well as in carbon monoxide. The other two affinities remained unsaturated or free. This view would allow the existence of innumerable isomeric derivatives. Thus two bodies, $CH_2 = CH_2$ and $CH_3 — \overset{//}{C}H$, could correspond to the formula C_2H_4, but only the first, ethylene, really exists. In addition to the true propylene, $CH_3 — CH = CH_2$, two other bodies, $CH_3 — CH_2 — \overset{//}{C}H$ and $CH_3 — \overset{//}{C} — CH_3$, could correspond to the formula C_3H_6. The preparation of such isomerides has been fruitless. The compound CH_2, methylene (see this), cannot be made. In the case of all sufficiently well-studied unsaturated compounds, it is established that the two free valences *invariably belong to two different carbon atoms.* By adding two atoms of chlorine to ethylene, $CH_2 = CH_2$, there arises the compound $CH_2Cl — CH_2Cl$; the isomeride $CH_3\overset{//}{C}H$, should yield $CH_3 — CHCl_2$. Inversely, we get ethylene, $CH_2 = CH_2$, from its chloride, $CH_2Cl — CH_2Cl$, while the isomeric, so-called ethylidene, $CH_3\overset{//}{C}H$, cannot be obtained from ethylidene chloride, $CH_3 — CHCl_2$. If really, as above supposed, the free affinities of the two carbon atoms are combined with each other—if double union occur—it cannot be asserted with certainty, and it is entirely irrelevant, as we possess no representation as to the nature of the union. It is doubtless certain that the possibility of the so-called free valence of a carbon atom is influenced by the free valence of another atom, which is in *direct* union with the first. It is very likely there exists $CH_3 - \overset{|}{C}H_2 - \overset{|}{C}H_2$ (propylene), but not the forms $CH_3 - CH_2 - \overset{/\!/}{C}H$ or $CH_3 - C - CH_3$. This knowledge accords with the actual facts, and considerably limits the number of possible isomerides. It finds expression in the supposition of the constant tetravalence of carbon. If new isomerides are discovered in the future, the assumption of the divalence of carbon can be admitted. So long, however, as convincing reasons are not present, we must refrain from introducing a new, fundamental, and far-reaching hypothesis, which would remove the existing regularities.

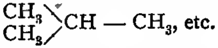
In the preceding pages we have discussed the different ways in which the carbon atoms are bound to each other in their hydrogen derivatives. We meet these in all other carbon compounds that may be regarded as derivatives of the hydrocarbons, resulting from the replacement of hydrogen by other elements or groups.

Since all the facts go to prove that the four valences of the carbon atom are similar (p. 38), isomerisms in similar carbon nuclei can take place only when the entering elements or groups attach themselves to carbon atoms with different functions; or, as ordinarily expressed, when they occupy different *chemical positions*. The following examples serve to illustrate:—

According to the formula C_2H_5Cl, there can be but one body of the structure $CH_3 - CH_2Cl$, because, in the original substance $CH_3 - CH_3$, dimethyl, both carbon atoms act alike. On the other hand, two isomeric bodies of the structure—

$$CH_3 - CH_2 - CH_2Cl \text{ and } CH_3 - CHCl - CH_3,$$

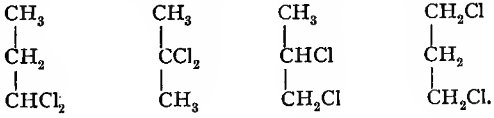
correspond to the formula C_3H_7Cl, because, in propane, $CH_3 - CH_2 - CH_3$, from which they originate, the carbon atoms are not similarly united, consequently, the entering halogen atoms can occupy relatively different positions. Thus, too, four isomerides correspond to the formula C_4H_9Cl, two springing from normal butane, $CH_3 - CH_2 - CH_2 - CH_3$, and two from isobutane—



$$\begin{array}{l} CH_3 \diagdown \\ CH_3 \diagup \end{array} CH - CH_3, \text{ etc.}$$

The number of isomerides is further increased by the entrance of two or several similar or dissimilar atoms or groups. For the formula $C_2H_4Cl_2$ we have two isomerides:—$CH_2Cl - CH_2Cl$ and $CH_3 - CHCl_2$.

For the formula $C_3H_6Cl_2$ four structural cases are possible:—



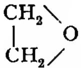
$$\begin{array}{l} CH_3 \\ | \\ CH_2 \\ | \\ CHCl_2 \end{array} \qquad \begin{array}{l} CH_3 \\ | \\ CCl_2 \\ | \\ CH_3 \end{array} \qquad \begin{array}{l} CH_3 \\ | \\ CHCl \\ | \\ CH_2Cl \end{array} \qquad \begin{array}{l} CH_2Cl \\ | \\ CH_2 \\ | \\ CH_2Cl. \end{array}$$

All other possible isomerides are derived in the same manner. The nature of the atoms or groups entering is immaterial as far as the isomeric relations (p. 38) are concerned.

Compounds obtained from the hydrogen derivatives by the replacement of hydrogen by halogens or the nitro group, NO_2, are usually designated *substitution products;* generally they retain the chemical character of the parent substance. In a broader sense, one can consider all carbon compounds as substitution derivatives of the hydrocarbons, or of methane, CH_4.

Two bivalent elements like S and O can unite with C with either one or two valences. In the first case, they may be combined with one or two carbon atoms:—

$CH_3 — CH = O$
Aldehyde
Ethylidene Oxide.


Ethylene
Oxide.

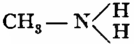
$CH_3 — O — CH_3$
Methyl Oxide, or
Dimethyl Ether.

If the bivalent element unite with but one affinity to carbon, the other must be saturated by some other element:—

$CH_3 — CH_2 — OH$
Ethyl Alcohol.

$CH_3 — CH_2 — SH.$
Ethyl Mercaptan.

Likewise, the trivalent elements, like nitrogen and phosphorus, may unite with carbon with all or with one affinity—either with one carbon atom—



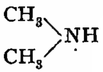
$$CH_3 — N\genfrac{}{}{0pt}{}{H}{H}$$

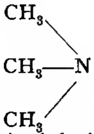
Ethylamine.

$CO = NH$
Carbimide.

$CH \equiv N$
Hydrogen
Cyanide.

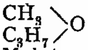
or with two or three carbon atoms:—


Dimethylamine.


Trimethylamine.

In this way two or more carbon atoms may be united to a molecule through the agency of an element of higher valence.

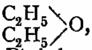
Those isomeric bodies (of like composition) containing several different carbon groups, held in combination by an atom of higher valence, are termed *metameric.* Examples are—



$$\genfrac{}{}{0pt}{}{CH_3}{C_3H_7}>O$$

Methyl-
propyl Ether.

and



$$\genfrac{}{}{0pt}{}{C_2H_5}{C_2H_5}>O,$$

Diethyl
Ether.

also

$$\left.\begin{matrix}CH_3\\CH_3\\CH_3\end{matrix}\right\}N \qquad \left.\begin{matrix}CH_3\\C_2H_5\\H\end{matrix}\right\}N \quad \text{and} \quad \left.\begin{matrix}C_3H_7\\H\\H\end{matrix}\right\}N$$

Trimethylamine. Methylethylamine. Propylamine.

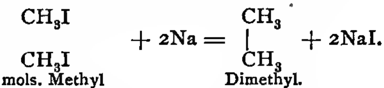
These can be resolved by various reactions into their component carbon groups (or their derivatives), and inversely be synthesized from these groups or their derivatives.

Law of Even Numbers.—In every carbon compound, the sum of the elements of uneven valence (of the monads and triads), like H, Cl, Br, and N, P, As, is an even number. Thus, in cyanuric acid, $C_3H_3N_3O_3$, the sum of the hydrogen and nitrogen atoms $= 6$; in ammonium trichloracetate, $C_2Cl_3 (NH_4)O_2$, the sum of the atoms of Cl, N and H $= 8$. This law, established empirically at first, and of importance in the deduction of chemical formulas, finds, at present, as observed in preceding lines, a simple explanation in the quadrivalent nature of carbon and the property of the elements to unite themselves by single affinities.

Radicals and Formulas.—Radicals or residues are atomic groups remaining after the removal of one or more atoms from saturated molecules. Ordinarily, *radicals* are groups containing carbon, while all others, like O, SH, NH_2, NO_2, are *residues* or groups. By the successive removal of hydrogen from the hydrocarbons of the formula C_nH_{2n+2}, radicals of different, increasing valence result. These may combine with other elements or groups until the form C_nH_{2n+2} is attained:—

	Molecules.	CH_4 Methane.	C_2H_6 Ethane.	C_3H_8 Propane.	C_4H_{10} Butane.
RADICALS.	univalent.	CH_3 Methyl.	C_2H_5 Ethyl.	C_3H_7 Propyl.	C_4H_9. Butyl.
	bivalent.	CH_2 Methylene.	C_2H_4 Ethylene.	C_3H_6 Propylene.	C_4H_8 Butylene.
	trivalent.	CH Methine.	C_2H_3 Vinyl.	C_3H_5 Glyceryl.	C_4H_7 Crotonyl.
	quadrivalent.	C Carbon.	C_2H_2 Acetylene.	C_3H_4 Allylene.	C_4H_6 Crotonylene.

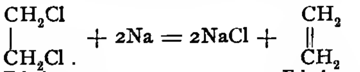
It may be observed from the preceding pages, that radicals are not capable of existing free. When the univalent radicals separate from their compounds they double themselves:—



$$\begin{array}{l} CH_3I \\ CH_3I \end{array} + 2Na = \begin{array}{c} CH_3 \\ | \\ CH_3 \end{array} + 2NaI.$$

2 mols. Methyl Iodide. Dimethyl.

The bivalent and quadrivalent radicals can only be isolated from their compounds when the affinities that are liberated belong to two adjacent carbon atoms—that is, those mutually uniting each other:—



$$\begin{array}{l} CH_2Cl \\ | \\ CH_2Cl\,. \end{array} + 2Na = 2NaCl + \begin{array}{c} CH_2 \\ \| \\ CH_2 \end{array}$$

Ethylene Chloride. Ethylene.

The radical $CH_3 - CH =$ cannot be isolated from $CH_3 - CHCl_2$ (comp. p. 42).

As in the examples just given, acetylene may be obtained from dichlorethylene:—

$$\begin{matrix}CHCl\\ \Vert \\ CHCl\end{matrix} + 2Na = \begin{matrix}CH\\ ||| \\ CH\end{matrix} + 2NaCl$$

Dichlorethylene. Acetylene.

The acceptance of radicals leads to a special nomenclature of the compounds. *Monochlorethane*, C_2H_5Cl, derived by substitution from the molecule of ethane, C_2H_6, may be viewed as a compound of the group ethyl with chlorine, hence, called *Ethylchloride*. $C_2H_2Cl_2$ is called *dichlormethane* or *methylene chloride;* $C_2H_5NH_2$ is known as *amidoethane* or *ethylamine*, etc. For this reason it is customary to ascribe especial names to the simpler and more frequently occurring radicals or atomic groups (see above). *Alcoholic radicals* or *alkyls* is the name applied to the univalent radicals C_nH_{2n+1}, from their most important compounds—the alcohols, $C_nH_{2n+1}OH$. Those groups that are bivalent are called *alkylens*, etc.

The univalent radicals are again distinguished as *primary*, *secondary* and *tertiary*, according as the unsaturated carbon atom is attached to one, two or three carbon atoms:—

$CH_3 - CH_2 - CH_2 -$

Primary Propyl.

$$\begin{matrix}CH_3\\ CH_3\end{matrix}\!\!>CH -$$

Secondary Propyl.

$(CH_3)_3C -$

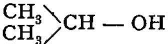
Tertiary Butyl.

These correspond to the primary, secondary and tertiary alcohols (see these).

Structural formulas are those indicating the complete grouping of all the atoms:—

$CH_3 - CH_2 - CH_2.OH$

Primary Propyl Alcohol.



$$\begin{matrix}CH_3\\ CH_3\end{matrix}\!\!>CH - OH$$

Secondary, or Isopropyl Alcohol.

They are a representation of the whole chemical deportment of a given compound. The rational or *constitutional formulas* only indicate the union of individual atoms—such as are especially characteristic of the compound. Thus, the formula $C_3H_7.OH$ indicates that the body is an alcohol; has properties common to all alcohols; it leaves undetermined, however, whether it is a primary or a secondary alcohol. For simplicity we employ such formulas and assign special names to the isomeric radicals. The *empiric* or *unitary* formula C_3H_8O affords no hint as to the character of the compound, since it belongs to an entire series of bodies that are isomeric, yet wholly different.

EARLY THEORIES RELATING TO THE CONSTITUTION OF THE CARBON COMPOUNDS.

The opinion that the cause of chemical affinity resided in electrical forces, came to light in the commencement of this century, when the remarkable decompositions of chemical bodies, through the agency of the electric current, were discovered. It was assumed that the elementary atoms possessed different electrical polarities, and the elements were arranged in a series according to their electrical deportment. Chemical union depended on the obliteration of different electricities. The *dualistic* idea of the constitution of compounds was a necessary consequence of this hypothesis. According to it, every chemical compound was composed of two groups, electrically different, and these were further made up of two different groups or elements. Thus, salts were viewed as combinations of electro-positive bases (metallic oxides), with electro-negative acids (acid anhydrides), and these, in turn, were held to be binary compounds of oxygen with metals and metalloids. (See Richter's Inorganic Chemistry.) With this basis, there was constructed the *electro-chemical, dualistic theory of Berzelius.* This prevailed almost exclusively in Germany, until about 1860.

The principles predominating in inorganic chemistry were also applied to organic substances. It was thought that in the latter complex groups (radicals) pre-existed, and played the same rôle that the elements did in mineral matter. Organic chemistry was defined as the chemistry of the compound radicals (Liebig, 1832), and led to the *chemical-radical theory*, which flourished in Germany simultaneously with the *electro-chemical* theory. According to this view, the object of organic chemistry was the investigation and isolation of radicals, in the sense of the dualistic idea, as the more intimate components of the organic compounds, and by this means they sought to explain the constitution of the latter.

In the meantime, about 1830, France contributed facts not in harmony with the electro-chemical, dualistic theory. It had been found that the hydrogen in organic compounds, could be replaced (substituted) by chlorine and bromine, without any apparent change in the character of the compounds. To the electronegative halogens was ascribed a chemical function similar to electro-positive hydrogen. This showed the electro-chemical hypothesis to be erroneous. The dualistic idea was superseded by a *unitary* theory. Laying aside all the primitive speculations on the nature of chemical affinity, the chemical compounds began to be looked upon as constituted in accordance with definite mechanical ground-forms —*types*—in which the individual elements could be replaced by others (early-type theory of Dumas, nucleus theory of Laurent). At the same time the dualistic view on the pre-existence of radicals was refuted. The correct establishment of the ideas, *equivalent, atom and molecule* (Laurent and Gerhardt), was an important consequence of the typical unitary idea of chemical compounds. By means of it a correct foundation was laid for further generalization. The molecule having been determined a chemical unit, the study of the grouping of atoms in the molecule became possible, and chemical constitution could again be more closely examined. The investigation of the reactions of double decomposition, whereby single atomic groups (radicals or residues) were preserved and could be exchanged (Gerhardt); the important discoveries of the amines or substituted ammonias by Würtz (1849), and Hofmann (1850); the epoch-making researches of Williamson, upon the composition of ethers, and the discovery of acid-forming oxides by Gerhardt— these all contributed to the announcement of the *type theory of Gerhardt* (1853), which was nothing more than an amalgamation of the early type or substitution theory of Dumas and Laurent with the radical theory of Berzelius and Liebig. The molecule was its basis—and to it there was attached a more extended grouping of the atoms in the molecule. The conception of radicals became different. They were no longer regarded as atomic groups that could be isolated and compared with elements, but as molecular residues which remained unaltered in certain reactions.

Comparing the carbon compounds with the simplest inorganic derivatives, Gerhardt referred them to the following principal fundamental forms or type:—

$$\begin{array}{cccc}
\left.\begin{array}{r}H\\H\end{array}\right\} & \left.\begin{array}{r}Cl\\H\end{array}\right\} & \left.\begin{array}{r}H\\H\end{array}\right\}O & \left.\begin{array}{r}H\\H\\H\end{array}\right\}N \\
\text{Hydrogen.} & \text{Hydrogen Chloride.} & \text{Water.} & \text{Ammonia.}
\end{array}$$

From these they could be obtained by substituting the compound radicals for hydrogen atoms. All compounds that could be viewed as consisting of two directly combined groups were referred to the hydrogen and hydrogen chloride types, *e. g.* :—

$$\begin{array}{ccccc}
\left.\begin{array}{r}C_2H_5\\H\end{array}\right\} & \left.\begin{array}{r}C_2H_5\\Cl\end{array}\right\} & \left.\begin{array}{r}CN\\H\end{array}\right\} & \begin{array}{c}C_2H_5\\CN\end{array} & \left.\begin{array}{r}C_2H_3O\\Cl\end{array}\right\} \\
\text{Ethyl Hydride.} & \text{Ethyl Chloride.} & \text{Cyanogen Hydride.} & \text{Ethyl Cyanide.} & \text{Acetyl Chloride.}
\end{array}$$

It is customary to refer all those bodies derivable from water by the replacement of hydrogen, to the water type; *i. e.*, those in which two groups are united by oxygen:—

$$\begin{array}{cccc}
\left.\begin{array}{r}C_2H_5\\H\end{array}\right\}O & \left.\begin{array}{r}C_2H_3O\\H\end{array}\right\}O, & \left.\begin{array}{r}C_2H_5\\C_2H_5\end{array}\right\}O & \left.\begin{array}{r}C_2H_3O\\C_2H_3O\end{array}\right\}O \\
\text{Alcohol.} & \text{Acetic Acid.} & \text{Ethyl Ether.} & \text{Acetic Anhydride.}
\end{array}$$

The compounds containing three groups united by nitrogen are considered ammonia derivatives:—

$$\begin{array}{cccc}
\left.\begin{array}{r}CH_3\\H\\H\end{array}\right\}N & \left.\begin{array}{r}CH_3\\CH_3\\CH_3\end{array}\right\}N & \left.\begin{array}{r}C_2H_3O\\H\\H\end{array}\right\}N & \left.\begin{array}{r}CO\\H\end{array}\right\}N
\end{array}$$

These types no longer possessed their early restricted meaning. Sometimes a compound was referred to different types, according to the transpositions the formula was intended to express. Thus aldehyde was referred to the hydrogen or water type; cyanic acid to the water or ammonia type:—

$$\left.\begin{array}{r}C_2H_3O\\H\end{array}\right\} \quad \text{and} \quad \left.\begin{array}{r}C_2H_3\\H\end{array}\right\}O, \qquad \left.\begin{array}{r}CN\\H\end{array}\right\}O \quad \text{and} \quad \left.\begin{array}{r}CO\\H\end{array}\right\}N$$

The development of the idea of polyatomic radicals, the knowledge that the hydrogen of carbon radicals could be replaced by the groups OH and NH_2, etc., contributed to the further establishment of *multiple* and *mixed types* :—

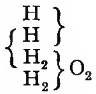
Compound Types :—

$$\begin{array}{ccc}
\left.\begin{array}{r}H_2\\H_2\end{array}\right\} & \left.\begin{array}{r}H_2\\H_2\end{array}\right\}O_2 & \left.\begin{array}{r}H_2\\H_2\\H_2\end{array}\right\}N_2
\end{array}$$

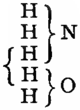
e. g. :—

$$\begin{array}{ccc}
\left.\begin{array}{r}Cl\\C_2H_4''\\Cl\end{array}\right\} & \begin{array}{r}\left.\begin{array}{r}H\\C_2H_4''\end{array}\right\}O\\ \left.\begin{array}{r}\\H\end{array}\right\}O\end{array} & \begin{array}{r}\left.\begin{array}{r}H_2\\CO''\end{array}\right\}N\\ \left.\begin{array}{r}\\H_2\end{array}\right\}N\end{array} \\
\text{Ethylene Chloride.} & \text{Ethylene Glycol.} & \text{Carbamide.}
\end{array}$$

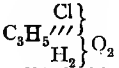
Mixed Types :—



$$\left\{\begin{array}{l} \left.\begin{array}{l} H \\ H \end{array}\right\} \\ \left.\begin{array}{l} H_2 \\ H_2 \end{array}\right\} O_2 \end{array}\right.$$

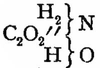


$$\left\{\begin{array}{l} \left.\begin{array}{l} H \\ H \\ H \end{array}\right\} N \\ \left.\begin{array}{l} H \\ H \end{array}\right\} O \end{array}\right.$$



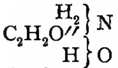
$$\begin{array}{r} \left.\begin{array}{r} Cl \\ C_3H_5{}''' \end{array}\right\} \\ \left.\begin{array}{r} H_2 \end{array}\right\} O_2 \end{array}$$

Chlorhydrin.



$$\begin{array}{r} \left.\begin{array}{r} H_2 \\ C_2O_2{}'' \end{array}\right\} N \\ \left.\begin{array}{r} H \end{array}\right\} O \end{array}$$

Oxamic Acid.



$$\begin{array}{r} \left.\begin{array}{r} H_2 \\ C_2H_2O'' \end{array}\right\} N \\ \left.\begin{array}{r} H \end{array}\right\} O \end{array}$$

Amido-acetic Acid.

The manner of arrangement finding expression in these multiple and mixed types was this: two or more groups were united into one whole—a molecule—by the univalent radicals. Upon comparing these typical with the structural formulas employed at present, we observe that the first constitute the transitional state from the empirical to the unitary formulas of the present day. The latter aim to express the perfect grouping of the atoms in the molecule. By granting a particular function to the atoms—their atomicity or valence—Kekulè (1858) indicated the *idea of types;* the existence and combining valence of radicals was explained by the tetravalence of the carbon atoms, and their tendency to mutually combine with each other, according to definite affinity units (Kekulè and Cooper). The type theory, consequently, is not, as sometimes declared, laid aside as erroneous; but it has only found generalization and amplification in a broader principle—just as the present structural theory will, at some future time, find wider importance in a more general hypothesis which encompasses the nature of chemical affinity.

RECENT VIEWS RELATING TO THE THEORY OF STRUCTURE.

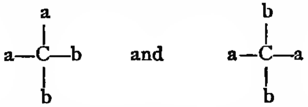
The theories now extant, relating to the manner in which the atoms are connected, do explain in a great measure the isomerisms and the behavior of carbon derivatives, yet they fail to give a complete picture, inasmuch as they do not touch, or even attempt to convey any idea as to the spatial relations of the atoms. Nor do they include any explanation of the nature of chemical affinity (p. 38). The instances, in which the ordinary structural formulas do not satisfy the actual relations, have become so numerous, that additions must be made to our structural theory, and many parts of it wholly recast. This cannot be deferred any longer. Two series of phenomena demand it.

The *one* series comprises all cases in which one and the same structural formula must be assigned two or more different compounds. Heretofore, such derivatives were regarded as *physical isomerides.* They were explained by assuming them to be different aggregations of molecules which were chemically similar. At present many different compounds are known to which one and the same structural formula must be assigned. For example, the two oxy-propionic acids, $CH_3.\ CH(OH).\ CO_2H$ (lactic acid, and sarco-lactic acid), the two acetylene dicarboxylic acids (fumaric and maleïc acids), the three dioxy-succinic acids (dextro-, laevo- and inactive tartaric acid), etc. Isomerides of this kind, different from the ordinary, may be formulated as *alloisomeric* bodies; the phenomenon is termed *alloisomerism* (Michael, *Ber.*, 19, 1384). An explanation, for these phenomena, has been sought in the spatial relations of the atoms, hence we speak of a spatial or *geometrical isomerism*, and of *stereochemical* formulas. For the term constitution or structure is substituted the phrase *configuration* of the molecules. The word *position* corresponds to the old term *union* (linking) (J. Wislicenus, p. 54).

In the *second* series of phenomena are included all compounds to which two different structural formulas may be rightly attributed. Such formulas are *tautomeric*. *Tautomerism* is explained by the assumption of motion of atoms between two positions (points) in equilibrio (Laar, p. 54).

STEREOCHEMICAL THEORIES.

As the assumption that the four atoms or groups, combined with one carbon atom, are arranged or lie in the same plane, leads to a far greater number of isomerides than are known, and as isomerides corresponding, *e. g.*, to the two planimetric and different atomic arrangements



$$\begin{array}{ccc} & \mathrm{a} & \\ & | & \\ \mathrm{a}- & \mathrm{C} & -\mathrm{b} \\ & | & \\ & \mathrm{b} & \end{array} \quad \text{and} \quad \begin{array}{ccc} & \mathrm{b} & \\ & | & \\ \mathrm{a}- & \mathrm{C} & -\mathrm{a} \\ & | & \\ & \mathrm{b} & \end{array}$$

have not been proved to exist, the structural theory makes no attempt to interpret spatial relations, but confines itself to the union of atoms in definite successive series. Le Bel and van't Hoff (1874)[*] were the first to demonstrate in what manner the actual relations might be made to harmonize with these representations. Their assumptions are embodied in the three following propositions:—

(1) The four affinities of the carbon atom, while separated in space, are arranged like the summits of the tetrahedron. The union of other atoms consists in the attachment of the same to these summits (tetrahedral angles). Hence, isomerides can only occur when the carbon atom is combined with four different monovolent groups. In such instances two isomeric derivatives C a b c d are possible. This is evident from an inspection of the tetrahedron model, and stands proved by the existence of, for example, two α-oxypropionic

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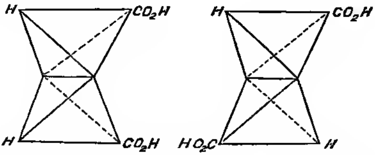
[*] van't Hoff-Herrmann: "Die Lagerung der Atome in Raum," 1877. van't Hoff: "Dix Années dans l'histoire d'une theorie." 1887.

acids, $CH_3.\mathit{C}H(OH).CO_2H$. Carbon atoms of this kind, linked to four different groups, are called *asymmetric* (represented by an italic *C*). This representation is chiefly employed by Le Bel and van't Hoff* to explain the optical rotatory power of the derivatives of carbon (p. 63).

(2) Single linking (union) between two carbon atoms occurs when two tetrahedra unite and have a pair of summits in common. The resulting form is a double pyramid, with six solid angles, to which the remaining six groups of the general formula, abcC — Cdef, attach themselves. This representation gives rise to a series of isomerides, greater in number than is known, or even probable; therefore van't Hoff assumes that the two tetrahedra, united with each other, rotate about a common axis, and that isomerism can only occur when the rotating systems are different. Compounds, with six different groups, abcC — Cdef, could then occur in four different forms. By doubling each of the three different groups—in accordance with the formula, abcC — Cabc, as in dioxy-succinic acid (tartaric acid) and dimethylsuccinic acid, three isomerides are possible for each. Compounds of the formula aabC — Cabc, as oxysuccinic or malic acid, can exist in two isomeric modifications each, etc., while succinic acid, $\begin{array}{l} CH_2.COOH \\ | \\ CH_2.COOH \end{array}$ (on rotating the octahedron), cannot possibly have any isomerides.

(3) The double linking (union) of two carbon atoms is represented by two tetrahedra having two summits in common (by an edge each.) The two previously rotating tetrahedra are now arrested, and isomerisms are therefore possible, where they could not formerly occur when they were united by single bonds. Thus, the compounds abC = Cab (or abC = Cac) must exist in two isomeric modifications each, the one in which similar groups are arranged upon the same side (maleïc acid), or that in which they are on opposite sides (fumaric acid):—



The same idea is expressed in a simpler way, as follows:—

$$(1)\quad \begin{array}{l} HC.CO_2H \\ \| \\ HC.CO_2H \end{array} \quad\text{and}\quad (2)\quad \begin{array}{l} HO_2C.CH \\ \qquad\| \\ \quad HC.CO_2H. \end{array}$$

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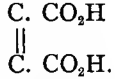
* *Ibid.*

The first formula allows maleïc acid to form an anhydride. Fumaric acid is not adapted thereto, because of the distance between the two carboxyls.

Triple union of two carbon atoms is represented by two tetrahedra, with three pairs of common summits (according to van't Hoff)—that is, each tetrahedron presents one of its plane surfaces. Geometrical isomerides are not possible for the compounds $aC \equiv Cb$. This is also the case with the structural formulas.

These ideas, first employed by Le Bel and van't Hoff almost exclusively for the purpose of explaining the optical activity of the carbon compounds (p. 63), have been given more recently a broader development, through the labors of J. Wislicenus*; they have been especially applied in the interpretation of chemical relations. This has been achieved by the introduction of two new theories bearing upon the manner (kind) of the additive-reactions of the unsaturated carbon compounds, and also upon the mutual influence of the groups in union with carbon.

For example, begin with acetylene dicarboxylic acid,

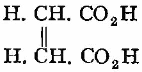


$$\begin{array}{l} C.\ CO_2H \\ \| \\ C.\ CO_2H. \end{array}$$

In this, the two carbon tetrahedra have three summits in common. When addition products are formed, the groups added must be attached upon the same sides of the tetrahedra (just as is the case with the two carboxyls). The addition of two hydrogen atoms, therefore, to the acetylene dicarboxylic acid would produce maleïc and not fumaric acid. In the stereochemical formulas corresponding to these acids (see above), the position of similarly named groups in formula 1 is designated *plane-symmetric*, in formula 2 (that of fumaric acid) it is called *central* or *axially-symmetric*. The positions on the same sides of the tetrahedra are also termed *corresponding*.

Additions occur with the "double linking" of carbon atoms, just the same as in the case of "triple linking." The added groups occupy corresponding positions. The addition of hydrogen to maleïc and fumaric acids gives rise to two different configurations:—

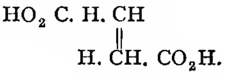
(1)



$$\begin{array}{l} H.\ CH.\ CO_2H \\ \quad \| \\ H.\ CH.\ CO_2H \end{array}$$

and

(2)



$$\begin{array}{r} HO_2\ C.\ H.\ CH \\ \| \quad \\ H.\ CH.\ CO_2H. \end{array}$$

corresponding to two isomeric succinic acids. When, however, the "double linking" is broken, the tetrahedra which, previously, were stationary, become movable and revolve about their common axis, and for this reason isomerism is impossible (according to van't Hoff). Wislicenus maintains, however, that singly-linked tetrahedra can become fixed in position, and that in consequence there will result

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* J. Wislicenus, *Ueber die räumliche Anordnung der Atome, 1887*.

a partial rotation (about 120°) of the same. This is induced by the mutual action or influence of the elements or groups in union with the carbon atoms, in which case like-named groups (positive or negative) repel, and those that are unlike, strive to approach one another. In the plane-symmetric formula (1) given above, the two carboxyls and the hydrogen atoms, occupying corresponding positions, repel each other and produce a rotation of the system, which reaches to the axially-symmetric position (formula 2). The latter configuration is the *preferable* one; therefore, the more stable, or the only one that really exists.

K. Auwers and V. Meyer* have made perfectly similar observations upon the "fixation" of two "singly-linked" tetrahedra. At the same time they call attention to the fact that compounds of the general formula aabC — Caab (*e. g.* benzil dioxime) can occur in three isomeric configurations.

By means of the representations just described, it is possible to interpret and explain the facts which, in many cases, fall far short of meeting satisfactory explanation from the structural theory. However, many and great difficulties yet remain;† so that, in applying the stereochemical views, reserve and caution should be used.

It should not be forgotten that even the new doctrine includes no explanation for, or representation of, the nature of chemical affinity; hence, like the structural formulas, it gives but an imperfect formulation of actual facts. The basis of this theory, that the "double" and "triple linking" is dependent upon a more intimate, therefore more stable position or arrangement of the atoms, is rather questionable, as it is well established that the unsaturated compounds possess greater specific volume, greater heat of combustion, less stability, etc., than those that are saturated (p. 57). Therefore, the stereochemical doctrine can only be regarded as an empirical amplification of the theory of atomic linking. Like the Ptolemaic epicycles, it can have but a restricted, temporary value.

V. Meyer and E. Riecke have also developed a hypothesis upon the linking of atoms (*Ber.*, **21**, 946); it, however, leaves the nature of chemical affinity undisturbed, and for that reason further deductions do not follow from it. A. Baeyer seeks to evolve a mechanical representation upon the polyvalent and ring-shaped union of the carbon tetrahedra by assuming the deviation of the points of attraction. The tensions thus induced correspond approximately to the variable stability and heat of combustion of these compounds (*Ber.*, **18**, 2278).

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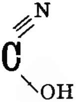
* *Ber.*, **21**, 790, 948, 3511.

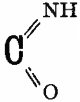
† Aronstein, *Ber.*, **21**, 2831; Hell, *Ber.*, **22**, 57; v. Miller, **22**, 1713; Michael, *Jour. pr. Chem.*, **38**, 1. Compare *Annalen*, **248**, 342; Anschütz, *Ann.*, **254**, 170; L. Meyer, *Ann.*, **247**, 251.

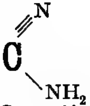
THE TAUTOMERIC THEORY.

Those cases in which, according to the structural theory, two formulas are possible, while but one corresponding compound is known, contradict the idea of alloisomerism. If we build up the compound corresponding to the formulas by means of synthetic reactions, two different products are not obtained. On the contrary, but one results. Conversely, such bodies frequently react, in different reactions, in two different directions as indicated by the formulas. Therefore, such formulas seem to be identical—*tautomeric*—and in tautomeric compounds the atoms appear to hold an alterable position (Laar, *Ber.*, 18, 730; Rathke, *Ber.*, 20, 1057). Examples of this class are:—


Cyanic Acid.

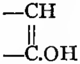
and


Isocyanic Acid.

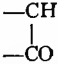

Cyanamide.

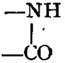
and


Carbdi-imide.

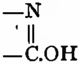

$$\begin{array}{l}—CH\\ \quad\|\\ —C.OH\end{array}$$
Hydroxylform.

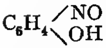
and


$$\begin{array}{l}—CH_2\\ \quad|\\ —CO\end{array}$$
Ketoneform.


$$\begin{array}{l}—NH\\ \quad|\\ —CO\end{array}$$
Lactam.

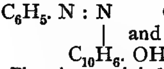
and


$$\begin{array}{l}—N\\ \quad\|\\ —C.OH\end{array}$$
Lactim.

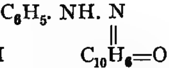

Nitrosophenol.

and


Quinone-oxime.


$$\begin{array}{r}C_6H_5.N:N\\ |\\ C_{10}H_6.OH\end{array}$$
Phenyl-azonaphthol.

and


$$\begin{array}{r}C_6H_5.NH.N\\ \|\\ C_{10}H_6{=}O\end{array}$$
Naphtho-quinone-phenylhydrazone.

From their formulas, these compounds are apparently different; in reality, they are identical. Laar assumes that the cause of this is to be ascribed to a mobile- (hydrogen) atom oscillating between two points in equilibrio, and thereby rendering the entire aggregation movable. This phenomenon Laar styles *tautomerism*, while others designate it *desmotropy* (*Ber.*, 21, 2228). The replacement of this hydrogen atom of tautomeric bodies by less mobile alkyls gives rise to the isomerides of the tautomeric compounds.

A. Baeyer opposes the preceding idea by maintaining that there is but one definite formula for each compound (*Ber.*, 16, 2188), and of the tautomeric forms but one will be stable while the other is unstable and can only exist in its derivatives. The latter form or modification is designated *pseudomeric* (see lactams and lactims). Hantzsch (*Ber.*, 20, 2801, 21, 1754), too, holds that every compound has but one definite structural formula. Tautomeric bodies (reacting in two directions) can exist in two "phenomenon-forms," corresponding to the tautomeric formulas; these are distinguished by physical characteristics, and are designated *desmotropic* conditions (see the ester of hydroquinone dicarboxylic acid). However, it is frequently impossible to fix upon any particular formula for a compound (see nitrosophenol), or to prove that it exists in two modifications. Tautomerism, therefore, appears to be the limit, and its desmotropism constitutes the gradual transition to isomerism (*Ber.*, **21**, 1857). In determining questions pertaining to tautomerism, those reactions only are applicable, from which electrolytic dissociation is excluded (Goldschmidt, *Ber.*, **23**, 253).

PHYSICAL PROPERTIES OF THE CARBON COMPOUNDS.

Usually we can foresee that the physical, as well as the chemical, properties of the derivatives of carbon must be conditioned by their composition and constitution. Such a regular connection, however, has been as yet only approximately established for a few properties. Those meriting consideration here, serving, therefore, chiefly for the external characterization of carbon derivatives, are the specific gravity in the gaseous and liquid condition, the melting and boiling temperatures, the behavior towards light, and electric conductivity.

SPECIFIC GRAVITY.

By this term is understood the relation of the absolute weights of equal volumes of bodies, in which case we take as conventional units of comparison, water for solids and liquids, and air or hydrogen for gaseous bodies (see p. 29).

For the latter, as we have already seen, the ratio of the specific gravity (gas density) to the chemical composition is very simple. Since, according to Avogadro's law, an equal number of molecules are present in equal volumes, the gas densities stand in the same ratio as the molecular weights. Therefore, the *specific volume*, *i. e.*, the quotient of the molecular weight and specific gravity, is a constant quantity for all gases (at like pressure and temperature). The relations are different in the cases of liquid and solid bodies. Since in the solid and liquid states the molecules are considerably nearer each other than when in the gaseous condition, the specific gravities cannot be, as with gases, proportional to the molecular weight, and are also modified by the size of the molecules and their distance from each other. The size and distance are unknown to us; the latter increases, too, with the temperature, therefore, the theoretical groundwork for deduction of specific gravities is far removed from us. However, some regularities have been empirically established for the specific gravity of *liquid* bodies. These appear, upon comparing the specific volumes or molecular volumes.

In determining the specific gravity of liquid compounds, a small bottle—a pyknometer—is used. Its contracted portion is provided with a mark; more complicated apparatus is employed where greater accuracy is sought (*Annalen*, 203, 4). Descriptions of modified pyknometers will be found in the Handwörterbuch v. Ladenburg, 3, 238. To get comparable numbers, it is recommended to make all determinations at a temperature of 20° C., and refer these to water at 4°, and a vacuum. Letting *m* represent the weight of substance, *v* that of an equal volume of water at 20°, then the specific gravity at 20° referred to water at 4°, and a vacuum (with an accuracy of four decimals), may be ascertained by the following equation (*Annalen*, 203, 8):—

$$d\,\frac{20}{4} = \frac{m\,.\,099707}{v} + 0.0012.$$

To find the specific volumes at the boiling temperature, the specific gravity at any temperature, the coefficient of expansion and the boiling point must be ascertained; with these data the specific gravity at the boiling point is calculated, and by dividing the molecular weight by this, there results the specific or molecular volume. Kopp's dilatometer (*Annalen*, 94, 257, compare Thorpe, *Journal Chem. Soc.*, 1880, 141, and Weger, *Annalen*, 221, 64), is employed in obtaining the expansion of liquids. For a method of getting the direct specific gravity at the boiling point, consult Ramsay, *Ber.*, 12, 1024; Schiff, *Ann.*, 220, 78, and *Ber.*, 14, 2761; also Schall, *Ber.*, 17, 2201, and Neubeck, *Zeit. phys. Chem.*, 1, 651.

H. Kopp ascertained that the following relations existed between the composition of carbon compounds and their molecular volumes at the boiling temperature:—

1. Isomeric compounds possess approximately like specific volumes.
2. Like differences in specific volume correspond to like differences in composition.

From these data arose the following law: the specific volume of a liquid compound (mol. volume), at its boiling point, is equal to the sum of the specific volumes of its constituents (of the atomic volumes). This gives to every element a definite atomic volume in its compounds.

In homologous compounds the difference, CH_2, corresponds to a difference of 22 in specific volume, for example:—

		Molecular Weight.	Specific Volume.	Difference.
Formic Acid..............	CH_2O_2	46	42	22
Acetic Acid...............	$C_2H_4O_2$	60	64	22
Propionic Acid...........	$C_3H_8O_2$	74	86	
Butyric Acid..............	$C_4H_8O_2$	88	108	22

The replacement of a carbon atom by two hydrogen atoms, does not cause any alteration in specific gravity, *e. g.*,—

		Molecular Weight.	Specific Volume.
Cymene...................	$C_{10}H_{14}$	134	187
Octane.....................	C_8H_{18}	114	187

As the specific volume of the group CH_2 equals 22, and the specific volume of one atom of C is equal to that of two hydrogen atoms, it follows that the specific volume of one carbon atom (its atomic volume) is 11, and that of one hydrogen atom 5.5. In a similar manner Kopp deduced two different atomic volumes for oxygen. If oxygen be in union with both affinities to one carbon atom (intra-radical), its atomic volume is equal to 7.8; but if it be combined (extra-radical) with two different atoms (as in $(C_2H_5)_2O$ and C_2H_5OH), its atomic volume is equal to 12.2. Hence, the specific volume of a compound of the formula $C_aH_bO_cO'_d$ (O represents intra- and O′ extra-radical oxygen) may be calculated from the equation:—

$$\text{Molecular Volume} = 11 \,.\, a + 5.5 \,.\, b + 12.2 \,.\, c + 78 \,.\, d.$$

The other elements exhibit similar definite specific volumes in their compounds, *e. g.*, chlorine = 22.8, bromine = 27.8, iodine = 37.5. Sulphur, like oxygen, has two values: the atomic volume of the intra-radical sulphur (in CS) equals 28.6; that of the extra-radical, 22.6. In ammonia and its derivatives, nitrogen has the specific volume 2.3, in the CN group 17, in NO_2, 8.6.

With such data the molecular volumes, and, of course, the specific gravities, can be obtained with approximate accuracy.

The most recent researches,* based upon an abundance of material, and at the same time giving due consideration to the structural relations of the carbon compounds, prove conclusively that the supposed regularities, mentioned above, are unfounded. The fact is, isomeric compounds in no manner have equal molecular volumes, and their atomic volumes are not constant (Lossen, *Ann.*, 213, 316). The volume for the difference CH_2 (see above) is not constant in the different homologous series, but varies, for example, in the esters of the fatty acids, from 19–28, and constantly increases with the higher members. Further, the hydrogen volume is not always 5.5, but it varies according to the manner in which it is derived (see *Ann.*, 233, 318; *Ber.*, 20, 767). The atomic volume of O is exceedingly variable (*Ann.*, 233, 322); at times the entrance of oxygen into compounds causes a decrease in volume (*Ber.*, 19, 1594):—

	Vol.		Vol.
Toluene, C_7H_8..................	103.8	Propyl Alcohol, C_3H_8O.........	73.4
Benzyl Alcohol, C_7H_8O......	102.1	Propyl Glycol, $C_3H_8O_2$..........	72.1

Another point to be considered is that the comparability of the sp. volumes of liquid bodies is not fixed by the boiling temperature, because the boiling points are dependent upon external pressure, and vary very widely in accordance with pressure. Consequently at temperatures other than that of boiling, similar but varying regularities were observed (Horstmann, *Ber.*, 19, 1579; Lossen, *Ann.*, 243, 101). Hence it is (1) that the molecular volumes in nowise represent the sums of the atomic volumes, (2) that the latter are scarcely determinable, (3) that the specific gravities and molecular volumes depend less upon the volume of the atoms, than upon their manner of linkage, and upon the structure of the molecules. Therefore to deduce regularities in the specific volumes it is first necessary to carefully consider the chemical structure of the compounds. For an exhaustive treatment of these relations, see Kopp, *Ann.*, 230, 1–117; *Ber.*, 22, Ref., 190. In this connection the influence of the double union of the C- atoms in the unsaturated compounds and the ring-form linking in the benzene derivatives, is significant. It has long been known (Buff) that the molecular volumes of the unsaturated compounds of the paraffin series were from 1.5–3 greater than those calculated by Kopp. Later research made them 4.4 (*Ann.*, 220, 298 and 221, 104), which has been confirmed by Horstmann's most recent investigations (*Ber.*, 19, 1591 and 20, 779). The divalent union is therefore less intimate (p. 41) and the unsaturated compounds consequently show a greater heat of combustion (*Ann.*, 220, 320).

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* Lossen and others: *Ann.*, 214, 81, 138; 221, 61; 224, 56; 225, 109; 233, 249, 316; R. Schiff, *Ann.*, 220, 113, 278; Horstmann, *Ber.*, 19, 1579; 20, 766 and 21, 2211. Lossen, *Annalen*, 243, 1-103.

In the conversion of benzene hydrocarbons into their hydrides there is an increase in volume which is three times as great as in the conversion of the olefines into their corresponding paraffins. This would emphasize the theory that in the benzene nucleus there are three doubly combined carbon atoms (*Ann.*, 225, 119 and *Ber.*, 20, 771). The specific gravities of the benzene hydrides is notably greater (consequently the molecular volumes are smaller) than their corresponding olefines, and that accounts for the fact that in the ring-linking of the C- atoms in the benzene nucleus there is an appreciable contraction in volume (*Ann.*, 225, 114 and *Ber.*, 20, 773). For further investigations relating to the benzene derivatives see Horstmann, *Ber.*, 21, 2211, and Neubeck, *Zeit. phys. Chem.*, 1, 649.

MELTING POINTS—BOILING POINTS.

Every pure carbon compound, if at all fusible or volatile, exhibits a definite melting and boiling temperature. It is customary to determine these for the characterization of the substance.

Boiling Points. These are determined in a so-called boiling flask, *i. e.*, a small flask with wide neck, and provided on the side with an exit tube. The thermometer is fixed in the opening of the neck by means of a cork. It should not be allowed to dip into the liquid; it must only be surrounded by the vapors.

In accurate determinations it is necessary to apply corrections to the indicated temperatures. If a thermometer is not wholly immersed in vapor, but as ordinarily happens, is partly extended into the air beyond the distillation vessel, the external mercury column will not be heated the same as that on the interior, hence the recorded temperature will be less than the real. The necessary correction will be reached with sufficient accuracy by adding to the observed temperature the quantity $n\,(T - t).\,0.000154$. Here n indicates the length of the mercurial column without the vessel, in degrees of the thermometer, T the observed temperature, t the medium temperature of the air about the external column of mercury (this is approximately ascertained by holding a second thermometer about the middle of the exposed part); 0.000154 is the apparent coefficient of expansion of mercury in glass. The correction is best avoided by having the entire mercurial column played upon by the vapors of the liquid. Pawlewski has presented a simple device to effect this (*Berichte*, 14, 88). It is also applicable in cases where but small quantities of liquid are employed.

If the barometric column did not indicate a normal pressure of 760 mm. during the distillation a second correction in the observed boiling temperature is necessitated. This is ordinarily accomplished by either adding to or deducting from the observed temperature 0.1° C. for a difference of every 2.7 mm. between the observed and normal barometric height (760 mm). This correction is, however, very inaccurate, because the differences between pressure and boiling point vary widely for each body (*Ber.*, 20, 709). To avoid this correction it is advisable to reduce the pressure in the apparatus to the normal. The pressure regulators of Bunte (*Ann.*, 168, 139) and Lothar Meyer (*Ann.*, 165, 303) are adapted to this purpose. In distilling under any pressure the forms of apparatus devised by Staedel and Schuhmann (*Ann.*, 195, 218 and *Ber.*, 13, 839) will be found very serviceable. For a method, applicable in determining the boiling points of very small amounts of liquids, see *Ber.*, 19, 794.

Liquids of different boiling points are separated by *fractional distillation*, an operation performed in almost every distillation. The portions passing over between definite temperature intervals (from 1–10°, etc.) are caught apart and subjected to repeated distillation, the portions boiling alike being united. To attain a more rapid separation of the rising vapors, these should be passed through a vertical tube. In this the vapors of the higher boiling compound will be condensed and flow back, as in the apparatus employed in the rectification of spirit. To this end there is placed on the boiling flask a so-called *fractional* tube of Würtz. Excellent modifications of this have been described by Linnemann, Le Bel, Hempel and others. For the action of these boiling tubes see *Ann.*, 224, 259; *Ber.*, 18, Ref. 101, and *Ann.*, 247, 3. It is often required to perform the distillation in vacuo; and this is best effected by exhausting the boiling chamber. An apparatus answering this purpose is mentioned in *Berichte*, 9, 1870. A very simple contrivance, regulating the pressure at the same time, is that described by F. Krafft (*Berichte*, 15, 1693; 22, 820). Also consult Thorne and Godefroy, *Ber.*, 16, 1327, and 17, Ref. 159; as well as Anschütz, "Distillation under reduced pressure," 1887. Vessels designed for the collection of the distillates have been described by L. Meyer, *Ber.*, 20, 1833, and Brühl, *Ber.*, 21, 3339.

The connection between the boiling points and chemical constitution of compounds will be discussed later in the several homologous groups. Generally the boiling point rises with the complication of the molecule. The unsaturated compounds boil at a higher temperature than those that are saturated. With isomerides having an equally large carbon nucleus those of normal structure possess the highest boiling points. These fall with the accumulation of methyl groups.

It may also be noted that the lower boiling isomerides possess a greater specific volume (*Ber.*, 15, 2570).

Melting Points. To determine these, introduce the substance into a thin, drawn-out tube, sealed at one end. This is attached to a thermometer and allowed to dip into a small beaker containing water, or a high boiling compound—paraffin. The beaker is warmed upon a sand bath until the substance in the little tube melts, and the temperature noted. For convenient apparatus for this purpose, see *Berichte*, 10, 1800.

The greater part of the mercury column of the thermometer extends beyond the heated bath, and therefore receives less heat. In all accurate determinations, a correction for this is consequently necessary. This is done as described with the boiling temperature. Correction for barometric pressure is not required, because the melting points are but slightly affected by pressure.

See *Ber.*, 19, 1970, for a device intended for the direct determination of the corrected melting point. The melting point is generally rather high if the melting tube is very narrow. The most accurate results are obtained when larger quantities of material are used in the determination (*Ber.*, 21, Ref. 638).

Very often slight admixtures, which can hardly be excluded, even by fractional crystallization, will materially lower the melting point.

The relation between the melting point and the chemical constitution will be more fully considered under the different homologous groups of bodies.

OPTICAL PROPERTIES.

Refraction. The carbon compounds (like all transparent substances) possess a variable light refracting power. In this case, as in other cases, the quotient of the sine of the angle of refraction (r) into the sine of the angle of incidence (i) is a constant quantity for each substance. This number is termed the *coefficient of refraction*, or *refractive index* (n):—

$$\frac{\sin i}{\sin r} = n$$

The refractive index of liquids is mostly determined by two methods. In the one the deviation of a ray of light is noted when it passes through a cylinder filled with the liquid under examination. The spectrometer of Meyerstein is especially adapted to this purpose. The second method (that of Wollaston) is less accurate, but much simpler than the first. It is also applicable to small amounts of substance. It is based on the total refraction caused by a layer of liquids. This is determined by means of the refractometer of Pulfrich and Abbé.

The coefficient of refraction (n) varies with the temperature, consequently also with the specific gravity of the liquid.

Their relation was formerly assumed to correspond to the formula $\frac{n-1}{d}$, in which d represented the sp. gr. of the liquid for a given temperature. It is an almost constant quantity for all temperatures, and is called the *specific refractive power*. However, later research has proved that the theoretically deduced equation, $\frac{n^2-1}{(n^2+2)d}$ (the so-called n^2-formula), more nearly represents the actual facts (*Ber.*, 19, 2760). It is therefore, at present, applied almost exclusively.*

On comparing the refractive constants (using the $n - 1$ or n^2— formula) of a mixture of several liquids with those of the constituents, it will be discovered that the first equals the sum of the refractive constants of the latter, and corresponds to their

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* For a more accurate representation of these relations, see Landolt, *Pogg. Ann.*, 123, 595; *Ber.*, 15, 1031; Brühl, *Ber.*, 19, 2746 and 2821; *Ann.*, 235, 1, and 236, 233; *Ber.*, 20, 2288, and *Zeit. phys. Chem.*, 1, 307; Wiegmann, *Zeit. phys. Chem.*, 1, 218 and 257; Ketteler, *ibid.*, 2, 905.

The refractive index (n) can be referred to any wave-length that may be desired. Since, however, different substances have different dispersive power, such indices are not directly comparable, and they were, therefore, referred to rays of infinite wave-length (according to Cauchy's dispersion formula). The indices supposed to be freed from the influence of dispersion were represented by the letter A, and the refractive constants by $\frac{A-1}{d}$ and $\frac{A^2-1}{(A^2+2)d}$. The most careful investigations have shown that these assumptions possess neither theoretical nor empirical value, and on that account it is necessary to come back to the refraction of one definite ray. Therefore, either the yellow sodium line (D of the sun's spectrum) or the red line of hydrogen Hα (C of the sun's spectrum) may be used.

percentage content in the mixture. A similar relation exists for chemical compounds. Designating the product of the specific refractive power of a compound R (according to n — or n^2 — formula), the molecular weight M as the *molecular refraction*, and the product of the refractive index of the elements and their atomic weights, the *atomic refraction*, the proposition would read: "The molecular refraction of a liquid carbon compound is equal to the sum of the atomic refractions," corresponding to the equation :—

$$MR = amr + bm'r' + cm''r'',$$

in which a, b, c, represent the number of elementary atoms in the compound. The atomic refractions of the elements are deduced from the molecular refractions of the compounds obtained empirically, in the same manner as the atomic volumes are obtained from the molecular volumes (see p. 57).

While it was formerly assumed that but one atomic refraction existed for each element in its compounds, later researches have proved that the atomic refraction of the polyvalent elements is influenced by their manner of union. The following atomic refractions have been calculated for the red hydrogen ray, H*a*, and the formula $\frac{n^2-1}{(n^2+2)d}$ (*Brühl, Ann.*, 235, 35, and Conrady, *Ber.*, 32, Ref. 224); "singly linked" carbon has the atomic refraction* (r_a) equal to 2.48, hydrogen 1.04. chlorine 6.02, bromine 8.95. Oxygen has two "atomic refractions." When it is united by one bond to carbon (as hydroxyl, and in ethers), the constant is 1.58 (1.52 and 1.68 for the line D), while in its double union (in $C=O$) it is 2.34. Similarly, sulphur exhibits two different values (*Ber.*, 15, 2878).

The deportment of double- and treble-linked carbon atoms is worthy of note. The double union ($C_2=$), according to Brühl, is 1.78 (for r_a), that of the triple union ($C_2\equiv$) 2.18, *i. e.*, if two carbon atoms are "doubly linked," their atomic refraction equals $2\times2.48+1.78=6..74$, while in triple union it is $4.96+2.18=7.14$.

These relations have met with frequent application in the decision of questions pertaining to chemical constitution. Thus the greater molecular refraction (by $3\times1.78=5.34$ units) of the benzene bodies, confirms the view previously deduced from chemical facts, that there is present in the benzene nucleus three "double-linked" carbon atoms (*Ber.*, 20, 2288). However, the regularities noted above only hold good for bodies with slight dispersive power (the fatty bodies). In the case of substances possessing a greater dispersive power than cinnamyl alcohol, the molecular refraction is valueless for the determination of chemical structure (*Ber.*, 19, 2746).

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* The molecular refraction of a ray of indefinite wave-length (index A) is designated by R_A, the atomic refraction by r_A.

Rotation of the Plane of Polarization.*—Many carbon compounds, liquid and solid, are capable of rotating the plane of polarized light. These are chiefly naturally occurring substances, like the various vegetable acids, amyl alcohol, the sugars, carbohydrates and glucosides, the terpenes and camphors, alkaloids and albuminoids; they are said to be *optically active.* The rotation (of the angle α) is proportional to the length l of the rotating plane, hence, the expression $\frac{\alpha}{l}$ is a constant quantity. To compare substances of different density, in which very unequal masses fall upon the same plane, these must be referred to like density, and hence, the rotation must be divided by the sp. gr. of the substance at a definite temperature. The expression $\frac{\alpha}{l \cdot d} = [\alpha]$, in which the length of the rotating plane is given in decimeters, is called the *specific rotatory power* of a substance at a definite temperature and is designated by $[\alpha]_D$ or $[\alpha]_j$, according as the rotation is referred to the yellow sodium line D or the transitional color j. For solid, active substances, with an indifferent solvent, the expression $[\alpha] = \frac{100\,\alpha}{p \cdot l \cdot d}$ will answer; in this p represents the quantity of substance in 100 parts by weight of the solution, and d represents the specific gravity of the latter.

The specific rotatory power is constant for every substance at a definite temperature; it varies, however, with the latter, and is also influenced more or less by the nature and quantity of the solvent. Therefore, in the statement of the specific rotatory power of a substance, the temperature and the percentage amount of the solution must be included. By investigating a number of solutions of different concentration, the influence of the solvent may be established and the true specific rotation or the true rotatory constant of the pure substance, designated by A_D, may then be calculated. The product of the specific rotatory power and the molecular weight *p* divided by 100 is designated the molecular rotatory power:—

$$[M] = \frac{P\,[\alpha]}{100}$$

Consult *Ber.*, 21, 191, 2586, 2599, upon the influence of inactive substances on the rotatory power.

In crystalline substances, the rotatory power is connected with the crystalline form, and is usually conditioned by the existence of hemihedral planes (*see* Tartaric Acids). As the activity of most of them is retained by solution, or is then first perceptible, it is supposed that *crystal molecules* exist in the solution, and that these consist of a union of several chemical molecules. Since, further,

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* Compare Landolt, "Das optische Drehungsvermögen," 1879.

numerous solids and liquids are known in dextro- and lævo-rotatory and inactive modifications, in which we can detect no difference in chemical structure, besides the active modifications mostly convertible into inactive, it was concluded that the activity was caused not by single chemical molecules, but by groups of *physical molecules*. These were termed *physical isomerides*. Since we have ascertained that turpentine oil and camphor, in the form of vapor, possess the same specific rotatory power as when they are in the liquid or solid state, and inasmuch as optically different substances, having the same structural formula, possess the same molecular weight, it can no longer be doubted that the activity is induced by a peculiar, chemical atomic-grouping, which finds no expression in the structural formulas usually offered. Le Bel and van't Hoff * deserve the credit of having advanced a theory, based on the spatial relations of atoms, that succeeds in bringing the latter and the optical rotatory power into full harmony.

According to this theory, the activity of the carbon compounds is dependent upon the presence of *asymmetric* carbon atoms, *i. e.*, such as are combined with different atoms or atomic groups.

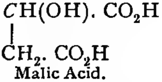
In all cases of this nature, every compound C a b e d, having its four groups arranged like the four solid angles (summits) of a tetrahedron, can have two possible configurations, the one being nothing more than the reflected image of the other. These forms are not superposable. There are two corresponding isomerides for each of these forms. These all agree perfectly in their chemical behavior, and differ from each other only in their opposite rotatory power, and opposite hemihedral (enantiomorphous) crystalline forms (see Tartaric Acids).

The following are examples of those compounds in which *one* asymmetric carbon atom is present:—

$\mathrm{CH_3.}\,\mathit{C}\mathrm{H(OH)CO_2H}$
Ord. Lactic Acid.

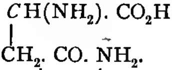
$\mathrm{C_2H_5.}\,\mathit{C}\mathrm{H(CH_3)CO_2H}$
Active Valeric Acid.

$\mathrm{C_2H_5.}\,\mathit{C}\mathrm{H(CH_3).\,CH_2OH}$
Active Amyl Alcohol.



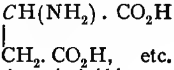
$$\begin{array}{l}\mathit{C}\mathrm{H(OH).\,CO_2H}\\ |\\ \mathrm{CH_2.\,CO_2H}\end{array}$$

Malic Acid.



$$\begin{array}{l}\mathit{C}\mathrm{H(NH_2).\,CO_2H}\\ |\\ \mathrm{CH_2.\,CO.\,NH_2.}\end{array}$$

Asparagine.



$$\begin{array}{l}\mathit{C}\mathrm{H(NH_2).\,CO_2H}\\ |\\ \mathrm{CH_2.\,CO_2H,}\end{array}$$

etc.

Aspartic Acid.†

Each of these compounds can occur in a *dextro-* and *lævo-* rotatory modification. What is more, the oppositely active forms can combine in equal quantities with each other, and produce an *inactive* double form, capable of re-solution into two active varieties (p. 64). Therefore, compounds containing *one* asymmetric carbon atom can give rise to *three* isomerides—two of which are active, and the third *inactive*, but capable of further division.

When two asymmetric carbon atoms are present in a compound, the number of possible isomerides is correspondingly greater. If the entire six groups in union with the two carbon atoms are different, corresponding to the general formula a b c C — C d e f, then four different configurations (p. 51) can exist, two of

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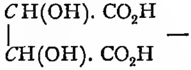
* van't Hoff, "Dix années dans l'historie d'une théorie," 1887.

† The asymmetric carbon atoms are indicated by an italic *C*.

which will be opposite and active. If each of the two carbon atoms are in union with three similar groups, as in tartaric acid—



$$\begin{array}{l} \mathit{C}\mathrm{H(OH).\,CO_2H} \\ | \\ \mathit{C}\mathrm{H(OH).\,CO_2H} \end{array} \quad —$$

three configurations are possible for each: a *dextro-* and *lævo-* form, as well as an *inactive* modification not capable of division. This is known as the *anti-modification;* in it the three groups are diametrically opposed to each other, and there results an inner compensation. Besides these there is also the *inactive* or *para-form*, resulting from the union of the two active varieties; this can be separated again into its components. Hence, tartaric acid may occur in *four* isomeric modifications, while malic acid yields but three isomerides (see above). The inactive form, capable of further division, is not possible in this instance.

Further research has fully confirmed the deductions of Le Bel and van't Hoff, so that at present it is an established fact that all known active substances contain asymmetric carbon atoms; conversely, it has repeatedly occurred that asymmetric compounds, previously known only in their active form, have been split up into their components (see tartaric acid, lactic acid, mandelic acid), while compounds, not asymmetric, have never yet undergone such a separation (*Ann.*, 239, 164).

On converting active substances into other derivatives, the activity is retained, providing asymmetric carbon atoms are present; when they disappear the derivatives are inactive. Thus, from the two active tartaric acids are derived the two corresponding active malic acids; whereas, the symmetrical succinic acid, obtained from the latter by further reduction, is inactive. Again, active amyl iodide affords an active ethylamyl and diamyl; on the other hand, an inactive amyl hydride (see Active Amyl Alcohol).

The asymmetric compounds, prepared by artificial means from inactive substances, are almost always inactive. This is explained by the fact that both modifications are found simultaneously and in like amounts; further, they also have the tendency to combine into inactive conglomerates. To this must be added that energetic reactions, or heat, tend to change the active into the inactive, decomposable variety (*e. g.*, dextro-tartaric acid changes at 175° into racemic acid); consequently the active variety formed is eventually changed to the inactive. Thus, when the albuminates are decomposed on heating them with baryta, the products are inactive leucine, tyrosine and glutamine, whereas at a lower temperature hydrochloric acid produces the active modifications (*Ber.*, 18, 358).

Artificially inactive, asymmetric compounds can be split into the two active forms. This splitting-up may sometimes be effected by the crystallization of salts, as was first demonstrated by Pasteur (1848) in the case of racemic acid. (See above.) This decomposition occurs at a fixed temperature, known as the *conversion temperature;* it is also dependent upon the solubility of the salts (*Ber.*, 19, 2148 and 2975).

The decomposition of inactive substances takes place more readily by the intervention of other active substances (especially cinchonine and quinine). This, too, was first observed by Pasteur with racemic acid. It seems to be due to the tendency of the active substance to unite itself exclusively with an active form of the inactive compound. By the employment of cinchonine not only racemic acid, but also malic, mandelic and tropaic acids have been thus split up. The splitting-up of inactive *α*-propyl piperidine into active conine, and that of methyl- and ethyl-piperidine, was effected through the use of active tartaric acid (*Ber.*, 20, 339).

A third procedure for the splitting-up of these derivatives is noteworthy; it depends upon the action of ferments—especially *Penicillium glaucum*—which results in the destruction of one of the active modifications. Under this treatment, racemic acid yields lævo-tartaric acid (Pasteur), inactive amyl alcohol passes into dextro-amyl alcohol, and methyl propyl carbinol and propylene glycol yield their lævo-rotatory modifications. *Penicillium glaucum* or *Bacterium termo* converts the synthetic, inactive mandelic acid into its dextro-rotatory form, while *Saccharomyces ellipsoideus* or Schizomycetes-fermentation produces the lævo-acid (*Ber.*, 16, 1568). Glyceric acid and ordinary lactic acid (*Ber.*, 16, 2721), as well as leucine and glutaminic acid, have sustained similar decomposition.

All these observations confirm the proposition of Le Bel and van't Hoff, that the asymmetrically constituted inactive carbon derivatives can be broken up into two oppositely active modifications.

ELECTRIC CONDUCTIVITY.

It is well known that substances capable of conducting electricity arrange themselves into two widely-separated groups: conductors of the first class, or those which conduct electricity without sustaining any change, and conductors of the second class, or those which constitute the electrolytes, and conduct only with their simultaneous separation into two *ions*. Conductivity can also be considered as a resistance, which the conductor opposes to the passage of the electricity. The customary measure of conductivity or resistance is the mercury unit. This is a column of mercury of one sq. mm. cross section, and one meter in length, at the temperature 0°.

Ostwald's investigations have demonstrated that the conductivity of electrolytes is intimately related to chemical affinity. It is a direct measure of the chemical affinity of acids and bases. Therefore, the determination of the conductivity of electrolytes (in aqueous solution), to which all organic acids and their salts belong, is of great interest and importance for all carbon derivatives.

Kohlrausch* has suggested a very simple and accurate means of determining the conductivity of electrolytes, which has been extensively applied by Ostwald.†

It is dependent upon the application of alternating currents, produced by an induction spiral, so that the disturbing influence of galvanic polarization is obviated.

The conductivity of electrolytes is not referred to the percentage content of their aqueous solutions, but (as the conductivity is ascertained by the equivalent ions) to solutions containing a molecule, or an equivalent of substance in grams. This value is the *molecular* (or equivalent) conductivity of the substance (*Zeit. phys. Chem.*, 2, 567).

The strong acids have the greatest molecular conductivity, then the fixed alkalies and alkali salts. Most organic acids, on the contrary

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* Wiedemann, *Ann.*, 11, 653.

† *Journ. pr. Chem.*, 32, 300, and 33, 353; *Zeit. phys. Chem.*, 2, 561.

(*e.g.* acetic acid) are poor conductors in a free condition, while their alkali salts approach those of the strong acids in conductivity. The molecular conductivity increases by about 2 per cent. per degree of temperature. It also increases with increasing dilution, and in the case of the poor conductors it is far more rapid than with the good conductors; in both instances it approximates a maximum (limiting) value. With good conductors this is attained at a dilution of 1000 litres to the gram-molecule; while with those poor in conducting power it is only reached when the dilution is indefinitely large. In fact, in such cases the conductivity is practically indeterminable.

An interesting observation in connection with the alkali salts of all acids is the variable increase of the molecular conductivity with increasing dilution. This is true both in the case of the strong and the weak acids (most organic acids belong to the latter class), and it varies according to their basicity. With sodium salts of monobasic acids, this increase equals from 10–13 units, by dilution of 32–1024 litres for the equivalent of substance, for the salts of dibasic acids from 20–25 units, for those of the tribasic 28–31, for those of the tetrabasic about 40, and those of the pentabasic about 50 units. Thus it may be seen that the increase in conductivity of acids, in their sodium salts, offers a means of determining the basicity and, consequently, the molecular magnitude of acids (Ostwald, *Zeit. phys. Chem.*, **1**, 74 and 97; **2**, 901; Walden, *Ibid.*, **1**, 530, and **2**, 49).

Molecular conductivity has acquired still greater importance by its application to the measurement of the dissociation of the electrolytes; it is at the same time the measure of the reactivity or chemical affinity, first, of acids, then bases, and, finally, of salts.

Arrhenius's electrolytic dissociation theory maintains that in aqueous solution the electrolytes are more or less separated into their ions; this would give a simple explanation for the variations of solutions from the common laws (under osmotic pressure, under the depression at the freezing point, etc.). The dissociation is also manifest in the molecular conductivity, for the latter is dependent upon the degree of dissociation and the speed of migration of the free ions; it is directly proportional to the quantity of the latter. Molecular conductivity increases with dilution and dissociation. When the latter is complete, it attains its maximum (μ_∞). The degree of dissociation (m) (or the fraction of the electrolyte split up into ions) for any dilution is found from the ratio of the molecular conductivity at this dilution (μ) to the maximum conductivity (for an indefinite dilution):—

$$\mathrm{m} = \frac{\mu}{\mu_\infty}.$$

The latter cannot be directly measured in the case of free organic acids, because most of them are poor conductors. But it can be obtained from the molecular conductivity of their sodium salts, by deducting from their maximum values the speed of migration of the sodium-ions (41.1), and adding those of the hydrogen-ions (285.8).

Since the molecular conductivity depends upon the dissociation of the electrolytes into their ions, their alteration by dilution of solution must proceed by the same laws as those prevailing in the dissociation of gases. This influence of dilution or volume (v) upon the molecular conductivity, or the degree of dissociation (m) is, therefore, expressed in the equation :—

$$\frac{m^2}{v(1-m)} = k,$$

which represents the law of dilution advanced by Ostwald (*Zeit. phys. Chem.*, **2**, 36 and 270). This law has been fully confirmed by the perfect agreement of the calculated and observed values (van't Hoff, *Zeit. phys. Chem.*, **2**, 777).

The value, k, is the same at all dilutions for every monobasic acid ; hence, it is a characteristic value for each acid, and is the measure of its chemical affinity. The determination of these chemical affinity-constants by Ostwald for more than 240 acids, has proved that they are closely related to the structure and constitution of organic acids (*Zeit. phys. Chem.*, **3**, 170, 241, 371).

SPECIAL PART.

The carbon derivatives may be arranged in two classes—the **fatty** and **aromatic** compounds. The name of the first class is borrowed from the fats and fatty acids comprising it. These were the first derivatives accurately studied. It would be better to name them marsh gas or methane derivatives, inasmuch as they all can be obtained from methane, CH_4. They are further classified into saturated and unsaturated compounds. In the first of these, called also paraffins, the directly united tetravalent carbon atoms are linked to each other by a single affinity.

The number of *n* carbon atoms possessing affinities capable of further saturation, therefore, equals $2n + 2$ (see p. 40). Their general formula is C_nX_{2n+2}. Here X represents the affinities of the elements or groups directly combined with carbon. The unsaturated compounds result from the saturated by the exit of an even number of affinities in union with carbon. According to the number of affinities yet capable of saturation, the series are distinguished as C_nX_{2n}, C_nX_{2n-2}, etc. (See p. 41.)

All the aromatic or *benzene* compounds contain a group consisting of six carbon atoms. The simplest derivative of this series is benzene, C_6H_6 (see p. 42). This accounts for the great similarity in their entire character. Their direct synthesis from the methane derivatives is only possible in exceptional cases; as a usual thing they cannot be converted into the series C_nH_{2n+2}. Their relatively great stability distinguishes them from the fatty bodies. They are generally more reactive, yielding, for instance, nitro-substitution products very readily, and forming various derivatives which the fatty compounds cannot possibly yield.

The recently investigated trimethylene and tetramethylene derivatives (see p. 42), with which may be included those of furfurol, thiophene and pyrrol, may be viewed as the transition stage from the methane compounds containing the open carbon chain, to those of benzene.

CLASS I.

FATTY BODIES, OR METHANE DERIVATIVES.

HYDROCARBONS.

The hydrocarbons show most clearly and simply the different manner in which the carbon atoms are bound to each other. We may regard them as the parent substances from which all other carbon compounds arise by the replacement of the hydrogen atoms by differents elements or groups.

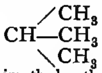
The outlines of the linking of carbon atoms were presented in the Introduction. In consequence of the equivalence (confirmed by facts) of the four affinities of carbon (see p. 38) no isomerides are possible for the first three members of the series C_nH_{2n+2}:—

CH_4 Methane. $CH_3 - CH_3$ Ethane. $CH_3 - CH_2 - CH_3$ Propane.

Two structural cases exist for the fourth member, C_4H_{10}:—

$CH_3 - CH_2 - CH_2 - CH_3$ Normal Butane.

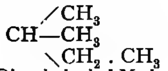
and



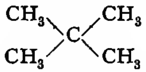
Trimethylmethane. (Isobutane.)

For the fifth member, pentane, C_5H_{12}, three isomerides are possible:—

$CH_3 - CH_2 - CH_2 - CH_2 - CH_3$ Normal Pentane.



Dimethyl-ethyl Methane. and



Tetramethyl Methane.

Hexane, C_6H_{14}, the sixth member, has five isomerides (see p. 75). With reference to the different formulation of these hydrocarbons see p. 72.

Formation of Hydrocarbons.—The higher paraffins can be gradually built up synthetically from methane, CH_4, yet not produced directly from their elements. Methane itself can be synthesized from carbon disulphide, CS_2 (produced by direct union of carbon and sulphur on application of heat) by passing the latter, in form of gas, together with hydrogen sulphide, over red-hot copper:—

$$CS_2 + 2H_2S + 8Cu = CH_4 + 4Cu_2S,$$

or by heating with phosphonium iodide, PH_4I; further, by the action of chlorine, carbon disulphide may be changed to carbon tetrachloride, CCl_4, and this reduced, by means of nascent hydrogen (sodium amalgam and water), to methane :—

$$CCl_4 + 4H_2 = CH_4 + 4HCl.$$

The direct union of carbon and hydrogen has only been observed in passing the electric spark between carbon points in a hydrogen atmosphere ; the product is acetylene, C_2H_2, which, with additional hydrogen (in presence of platinum black), becomes ethylene, C_2H_4, and then ethane, C_2H_8.

A universal method of producing the hydrocarbons consists in the dry distillation of complex carbon compounds, like wood, lignite and bituminous coal. At higher temperatures, *e. g.*, when their vapors are conducted through red-hot tubes, the hydrocarbons can condense to more complicated bodies, hydrogen separating. Thus, the compounds C_2H_6, C_2H_4, C_6H_8 (benzene), $C_{10}H_8$ (naphthalene), and others, are obtained from CH_4, methane.

A noteworthy formation of the hydrocarbons, especially the paraffins, is that of the action of hydrochloric acid or dilute sulphuric acid, and even steam, upon iron carbide.

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(1) PARAFFINS OR ETHANES.

$$C_n H_{2n+2}.$$

CH_4	Methane.	C_6H_{14}	Hexane.
C_2H_6	Ethane.	C_7H_{16}	Heptane.
C_3H_8	Propane.	C_8H_{18}	Octane.
C_4H_{10}	Butane.	C_9H_{20}	Nonane.
C_5H_{12}	Pentane.	$C_{10}H_{22}$	Decane, etc. (see p. 76).

There is no known limit to these hydrocarbons, or the number of carbon atoms attaching themselves to each other.

Formerly these hydrocarbons were designated as the hydrides of the corresponding monovalent radicals or alkyls: CH_3 (methyl), C_2H_5 (ethyl), C_3H_7 (propyl), etc. (see p. 45), because they were first obtained from compounds of these with other elements or groups. Hence the names methyl hydride for methane, ethyl hydride for ethane, etc. The most accessible and first known derivatives of the alkyls, C_nH_{2n+1}, were their hydroxides or alcohols as $C_2H_5.OH$, ethyl alcohol, and the halogen ethers of the latter.

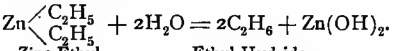
The following are the most important methods serving to convert the alkyl, C_nH_{2n+1}, derivatives into the corresponding hydrocarbons :—

1. Treat the alkylogens, $C_nH_{2n+1}Cl$ (readily produced from the alcohols, $C_nH_{2n+1}OH$), with nascent hydrogen. This may be done

by allowing zinc and hydrochloric acid, or sodium amalgam, to act upon the substance dissolved in alcohol:—

$$\underset{\text{Ethyl Chloride.}}{C_2H_5Cl} + H_2 = \underset{\text{Ethane. Ethyl Hydride.}}{C_2H_6} + HCl.$$

2. Decompose the zinc alkyl compounds with water or the mercury derivatives with hydrochloric acid (compare metallic compounds of the alcohol radicals):—



$$Zn\begin{cases}C_2H_5\\C_2H_5\end{cases} + 2H_2O = 2C_2H_6 + Zn(OH)_2.$$

Zinc Ethyl. Ethyl Hydride.

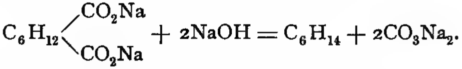
A more convenient mode of preparation is a combination of both methods: heat the iodides of the radicals with zinc and water, in sealed tubes, to 120°–180°.

3. A mixture of the salts of fatty acids (the carboxyl derivatives of the alkyls) and sodium or potassium hydroxide is subjected to dry distillation. Soda-lime is preferable to the last reagents:—

$$\underset{\text{Sodium Acetate.}}{CH_3CO_2Na} + NaOH = \underset{\text{Methane Methylhydride.}}{CH_4} + Na_2CO_3.$$

When the higher fatty acids are subjected to this treatment the usual products are the ketones; hydrocarbons, however, are produced when sodium methylate is used (*Ber.*, 22, 2133).

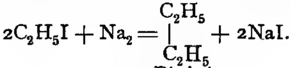
The dibasic acids are similarly decomposed:—



$$C_6H_{12}\begin{cases}CO_2Na\\CO_2Na\end{cases} + 2NaOH = C_6H_{14} + 2CO_3Na_2.$$

The hydrides of the radicals obtained by the preceding methods were distinguished from the so-called *free alcohol radicals*. These were prepared synthetically, as follows:—

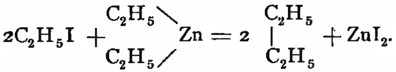
1. By the action of sodium (or reduced silver or copper) upon the bromides or iodides of the alcohol radicals in ethereal solution:—



$$2C_2H_5I + Na_2 = \begin{matrix}C_2H_5\\|\\C_2H_5\end{matrix} + 2NaI.$$

Diethyl.

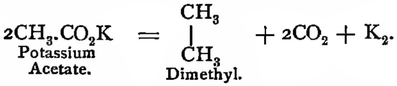
The iodides react in the same manner with the zinc alkyls:—



$$2C_2H_5I + \begin{matrix}C_2H_5\diagdown\\ \\C_2H_5\diagup\end{matrix}Zn = 2\begin{matrix}C_2H_5\\|\\C_2H_5\end{matrix} + ZnI_2.$$

2. By the electrolysis of the alkali salts of the fatty acids in concentrated aqueous solution: here, as in the decomposition of

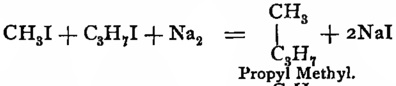
inorganic salts, the metal separates at the negative pole, decomposing water with liberation of hydrogen, while the hydrocarbons and carbon dioxide appear at the positive pole:—



$$2CH_3.CO_2K = \begin{matrix}CH_3\\|\\CH_3\end{matrix} + 2CO_2 + K_2.$$

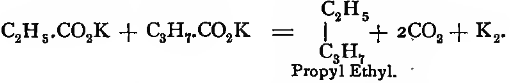
Potassium Acetate. Dimethyl.

Both synthetic methods proceed in an analogous manner, if a mixture of the iodides of two different alcohol radicals, or the salts of different acids, be employed:—



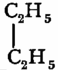
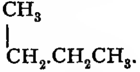
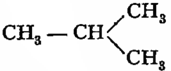
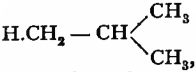
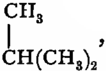
$$CH_3I + C_3H_7I + Na_2 = \begin{matrix}CH_3\\|\\C_3H_7\end{matrix} + 2NaI$$

Propyl Methyl.

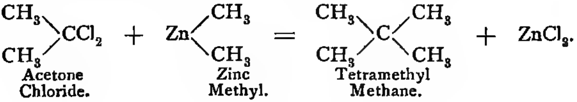


$$C_2H_5.CO_2K + C_3H_7.CO_2K = \begin{matrix}C_2H_5\\|\\C_3H_7\end{matrix} + 2CO_2 + K_2.$$

Propyl Ethyl.

It is known that the hydrocarbons obtained by these different methods are of similar composition and similar structure. Dimethyl is identical with ethyl hydride (ethane); diethyl with methyl propyl or butyl hydride (butane). This is evident from a consideration of the structural formulas. Thus, normal butane, $CH_3 - CH_2 - CH_2 - CH_3$, may be viewed as butyl hydride, C_4H_9H, or as diethyl,  $\begin{matrix}C_2H_5\\|\\C_2H_5\end{matrix}$, or propyl methyl,  $\begin{matrix}CH_3\\|\\CH_2.CH_2CH_3.\end{matrix}$ Isobutane, , can be regarded as isobutyl hydride,  or as isopropyl methyl,  $\begin{matrix}CH_3\\|\\CH(CH_3)_2\end{matrix}$, or trimethyl methane, $CH(CH_3)_3$, etc. Thus, the various syntheses of a given hydrocarbon may be deduced from its structural formula.

Of other synthetic methods we will yet mention the one employed in the preparation of quaternary hydrocarbons (p. 40). It consists in the action of the zinc alkyls upon acetone chloride and bodies similarly constituted:—



Acetone Chloride. Zinc Methyl. Tetramethyl Methane.

The ethanes arise in the dry distillation of wood, turf, bituminous shales, lignite and bituminous coal, and especially Boghead and cannel coal, rich in hydrogen; hence they are also present in illuminating gas and the light tar oils. Petroleum contains them already formed. They are, from methane to the highest hydrocarbon, almost the sole constituents of this compound.

The lowest members, up to butane, are gases, at ordinary temperatures, soluble in alcohol and ether. The intermediate members form colorless liquids of faint, characteristic odor, insoluble in water, but miscible with alcohol and ether. The higher members, finally, are crystalline solids (paraffins), soluble in alcohol, more readily in ether. The specific gravities of the liquid and solid hydrocarbons increase with the molecular weights, but are always less than that of water. The boiling points, too, rise with the molecular weights, and, indeed, the difference for CH_2 in case of similar structure of homologues, equals 30°, subsequently, with higher members it varies from 25°–13° (see p. 76). The isomerides of normal structure (p. 40) possess the highest boiling points; the lowest are those of the quaternary hydrocarbons. The general rule is—the boiling point of isomeric compounds falls with the accumulation of methyl groups in the molecule.

The paraffins are not capable of saturating any additional affinities; hence, they are not absorbed by bromine or sulphuric acid, being in this way readily distinguished and separated from the unsaturated hydrocarbons. They are slightly reactive and are very stable, hence, their designation as *paraffins* (from *parum affinis*). Fuming sulphuric acid and even chromic acid are without much effect upon them in the cold; when heated, however, they generally burn directly to carbon dioxide and water. When acted upon by chlorine and bromine they yield substitution products:—

$$CH_4 + Cl_2 = CH_3Cl + HCl,$$
$$CH_4 + 4Cl_2 = CCl_4 + 4HCl.$$

Other derivatives may be easily obtained by employing these products.

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(1) **Methane,** CH_4 (Methyl hydride), is produced in the decay of organic substances, therefore disengaged in swamps (marsh gas) and mines, in which, mixed with air, it forms fire damp.

In certain regions, like Baku in the Caucasus, and the petroleum districts of America, it escapes, in great quantities, from the earth. It is also present, in appreciable amount, in illuminating gas.

The synthesis of methane from CS_2 and CCl_4 was noticed upon page 69. It is most conveniently prepared by heating sodium acetate, in a glass retort, with 2 parts of soda-lime: $CH_3CO_2Na + NaOH = CH_4 + CO_3Na_2$.

Methane is a colorless, odorless gas, compressible under great pressure and at a low temperature; its critical temperature is —82°, and its critical pressure 55 atm. Its density equals 8 ($H = 1$) (or 0.5598, air = 1). It is slightly soluble in water, but more readily in alcohol. It burns with a faintly luminous, yellowish flame, and forms an explosive mixture with air:—

$$\underset{\text{1 vol.}}{CH_4} + \underset{\text{2 vols.}}{2O_2} = \underset{\text{1 vol.}}{CO_2} + \underset{\text{2 vols.}}{2H_2O}.$$

It is decomposed into carbon and hydrogen by the continued passage of the electric spark. When mixed with two volumes of chlorine it explodes in direct sunlight, carbon separating ($CH_4 + 2Cl_2 = C + 4HCl$); in diffused sunlight the substitution products CH_3Cl, CH_2Cl_2, $CHCl_3$ and CCl_4 are produced.

(2) **Ethane,** C_2H_6 (Ethyl Hydride, Dimethyl), is a colorless and odorless gas, condensable at 4° and a pressure of 46 atmospheres. Its formation from C_2H_5I, $(C_2H_5)_2Zn$, CH_3I and $CH_3.CO_2K$ corresponds to the general methods.

To prepare ethane, decompose zinc ethyl with water. It is obtained more conveniently by heating acetic anhydride with barium peroxide:—

$$2(C_2H_3O)_2O + BaO_2 = C_2H_6 + (C_2H_3O_2)_2\,Ba + 2CO_2.$$

The identity of the ethanes prepared by the various methods is ascertained from their derivatives, and confirmed by their similar heat of combustion (*Berichte*, 14, 501).

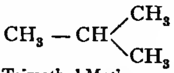
Ethane is almost insoluble in water; alcohol dissolves upwards of 1.5 vols. Mixed with an equal volume of chlorine it yields ethyl chloride, C_2H_5Cl, in dispersed sunlight; higher substitution products arise with excess of chlorine.

(3) **Propane,** C_3H_8, ethyl methyl, occurs dissolved in crude petroleum, and is most conveniently formed by the action of zinc and hydrochloric acid upon the two propyl iodides, C_3H_7I. It is a gas, but becomes a liquid below 17°. Alcohol dissolves upwards of six volumes of it.

(4) **Butanes,** C_4H_{10} (Tetranes). According to the rules of chemical structure, two isomerides correspond to this formula:—

(1) $CH_3—CH_2—CH_2—CH_3$

Normal Butane.

(2) 

$CH_3 - CH\left\langle\begin{matrix}CH_3\\ CH_3\end{matrix}\right.$

Trimethyl Methane.

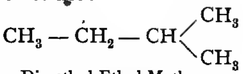
1. *Normal butane* (or diethyl, or propyl methyl, p. 72) occurs in crude petroleum, and is obtained synthetically by the action of zinc or sodium upon ethyl iodide, C_2H_5I. It condenses below 0° to a liquid, boiling at + 1°.

2. *Trimethyl methane* or isopropyl methyl, also termed isobutane, is prepared from the iodide of tertiary butyl alcohol, $(CH_3)_3CI$, by the action of zinc and hydrochloric acid. It condenses to a liquid at —17°.

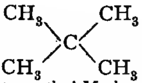
(5) **Pentanes,** C_5H_{12}. There are three possible isomerides :—

(1) $CH_3 — CH_2 — CH_2 — CH_2 — CH_3$

Normal Pentane.
B. P. 38°.

(2) 

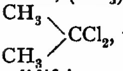
Dimethyl Ethyl Methane.
B. P. 30°.

(3) 

Tetramethyl Methane.
B. P. 10°.

1. *Normal pentane* exists in petroleum and the light tar oils of cannel coal, but has not been obtained by synthesis. It is a liquid, boiling at 37–39°, and having a specific gravity of 0.626 at 17°.

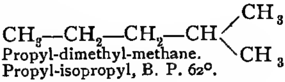
2. *Isopentane* is also present in petroleum, and is obtained from the iodide of the amyl alcohol of fermentation. It is a liquid, boiling at 30°; specific gravity = 0.638 at 14°.

3. *Tetramethyl methane* (quaternary pentane) is made by acting upon the iodide, $(CH_3)_3CI$, of tertiary butyl alcohol, or upon so-called acetone chloride,  $\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!CCl_2$, with zinc methyl (comp. p. 71). It is a liquid, boiling at 9.5°, and solidifying to a white mass at —20°. The addition of methyl groups constantly lowers the boiling point, but facilitates the transition to the solid state—raises the melting point.

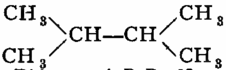
(6) **Hexanes,** C_6H_{14}. Five isomerides are possible :—

(1) $CH_3—CH_2—CH_2—CH_2—CH_2—CH_3$

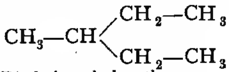
Normal Hexane.
Dipropyl, B. P. 71°.

(2) 

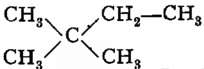
Propyl-dimethyl-methane.
Propyl-isopropyl, B. P. 62°.

(3) 

Di-isopropyt, B. P. 58°.

(4) 

Diethyl-methyl-methane.

(5) 

Tri-methyl-ethyl-methane, B. P. 43°–48°.

Four of these are known. *Normal hexane*, occurring in petroleum, may be obtained artificially by the action of sodium upon normal propyl iodide, $CH_3.CH_2.CH_2I$; by the distillation of suberic acid with barium oxide (p. 71); and further when nascent hydrogen acts on hexyl iodide, $C_6H_{13}I$ (from mannitol). It boils at 71.5°, and has the specific gravity 0.663 at 17°.

(7) **Heptanes,** C_7H_{16}. Four of the nine possible isomerides are known.

Normal heptane, $CH_3.—(CH_2)_5—CH_3$, is contained in petroleum and the tar oil from cannel coal. Together with octane it constitutes the chief ingredient of commercial ligroine (p. 77). It is produced in the distillation of azelaic acid, $C_9H_{16}O_4$, with barium oxide. It boils at 99°. Its specific gravity at 19° = 0.6967.

(8) **Octanes,** C_6H_{18}. Of the eighteen possible isomerides, two are known. Normal octane is present in petroleum and is obtained from normal butyl iodide,

C_4H_9I, by action of sodium (hence dibutyl), also from sebacylic acid, $C_{10}H_{18}O_4$, and from octyl iodide, $C_8H_{17}I$. It boils at 125°, and its specific gravity at 0° = 0.718.

The higher homologues occur in petroleum and tar oils, but cannot be isolated perfectly pure by fractional distillation. The different isomerides are obtained according to the methods already indicated. A series of normal paraffins in pure condition has been prepared by the reduction of the corresponding acids, $C_nH_{2n}O_2$, acetones, $C_nH_{2n}O$, and alcohols, $C_nH_{2n+2}O$ (of normal structure). The reduction of acids to paraffins ensues when the former are directly heated to 200–250° with concentrated HI and amorphous phosphorus; the acetones (ketones) must first be converted into the chlorides, $C_nH_{2n}Cl_2$, through the agency of PCl_5, and the alcohols also into chlorides, $C_nH_{2n+1}Cl$, and alkylens, C_nH_{2n}. The higher paraffins can be readily prepared by the action of sodium upon the methyl iodides. In this way the following normal paraffins have been obtained (F. Krafft, *Berichte*, 15, 1687 and 1711; 17, 2218).

		Melting Point.		B. P.	Sp. Gr.*
Nonane	C_9H_{20}	—51°		149.5°	0.7330
Decane	$C_{10}H_{22}$	—32°	Under 760 mm. pressure.	173°	0.7456
Undecane	$C_{11}H_{24}$	—26.5°		194.5°	0.7745
Dodecane	$C_{12}H_{26}$	—12°		214°	0.773
Tridecane	$C_{13}H_{28}$	—6.2°		234°	0.775
Tetradecane	$C_{14}H_{30}$	+4.5°		252.5°	0.775
Pentadecane	$C_{15}H_{32}$	+10°		270.5°	0.775
Hexdecane	$C_{16}H_{34}$	+18°		287.5°	0.775
Heptdecane	$C_{17}H_{36}$	+22.5°		303°	0.776
Octdecane	$C_{18}H_{38}$	+28°		317°	0.776
Nondecane	$C_{19}H_{40}$	+32°		330°	0.777
Eicosane	$C_{20}H_{42}$	+36.7°	Under 15 mm. pressure.	205°	0.777
Heneicosane	$C_{21}H_{44}$	+40.4°		215°	0.778
Docosane	$C_{22}H_{46}$	+44.4°		224.5°	0.778
Tricosane	$C_{23}H_{48}$	+47.7°		234°	0.778
Tetracosane	$C_{24}H_{50}$	+51.1°		243°	0.778
Heptacosane	$C_{27}H_{56}$	+59.5°		270°	0.779
Hentriacontane	$C_{31}H_{64}$	+68.1°		302°	0.780
Dotriacontane	$C_{32}H_{66}$	+70.0°		310°	0.781
Pentatriacontane	$C_{35}H_{72}$	+74.7°		331°	0.781

The higher normal paraffins, from hexdecane, $C_{16}H_{34}$, forward, are solids at ordinary temperatures, and crystallize readily from alcohol or ether. It is very remarkable that the specific gravities of the higher members are almost equal at their melting points, consequently the molecular volumes are nearly proportional to the molecular weights (*Berichte*, 15, 1719). Compare *Ann.*, 223, 268.

The highest paraffin that has yet been obtained is *Hexacontane*, $C_{60}H_{122}$, or *Dimyricyl*. It is produced when potassium or sodium acts upon myricyl iodide, $C_{30}H_{61}I$ (from myricyl alcohol). It dissolves with difficulty in alcohol and ether, and separates in the form of a white powder from benzene and chloroform. It melts at 102°, and when distilled, even in vacuo, sustains a partial decomposition (*Ber.*, 22, 502).

The higher members of this series are contained in petroleum and the tar oils produced in the distillation of turf, lignite and

---

* The specific gravities correspond to the temperatures at which the bodies melt (for nonane and decane at 0°).

bituminous coal. To isolate them in a pure condition, crude petroleum or the light tar oils are treated with concentrated sulphuric acid, which dissolves the non-saturated hydrocarbons, *e.g.*, C_nH_{2n}, and those of the benzene series (in tar oil) and destroys other organic substances. The separated oil is further treated with fuming nitric acid and sodium hydroxide, washed with water, dried, and fractionated over metallic sodium. In this way a whole series of hydrocarbons is obtained. Two series of hydrocarbons have been isolated from that fraction of American petroleum that boils from 0°–130°. The members of the first series possess normal structure:—

C_4H_{10}	0°	——	——
C_5H_{12}	38°	C_5H_{12}	30°
C_6H_{14}	71°	C_6H_{14}	61°
C_7H_{16}	99°	C_7H_{18}	91°
C_8H_{18}	125°	C_8H_{18}	118°

The members, C_9H_{20} to $C_{16}H_{34}$ (boiling at 270°), separated from the higher fractions, have not been obtained perfectly pure.

Petroleum or rock-oil (naphtha) was probably produced by the dry distillation of coal beds, caused by the earth's heat, or more probably by that of the fatty constituents of fossil animals (see Engler, *Ber.*, **21**, 1816). It occurs widely distributed in the upper strata of the earth—in Italy, Hungary, Gallicia, and in very considerable quantities in the Crimea and the Caucasus (on the shore of the Caspian). Its occurrence in Alsace and Hanover is not very extensive. It is obtained in remarkably large quantities in North America (in Pennsylvania and Canada) by boring. In a crude condition, it is a thick, oily liquid, of brownish color, with greenish lustre. Its more volatile constituents are lost upon exposure to the air; it then thickens and eventually passes into asphaltum. The greatest differences prevail in the various kinds of petroleum; it is only of late years that their thorough study has been commenced.

American petroleum consists almost exclusively of normal paraffins; yet minute quantities of some of the benzene hydrocarbons (cumene and mesitylene) appear to be present. In a crude form it has a specific gravity of 0.8–0.92, and distils over from 30–360° and beyond this. Various products, of technical value, have been obtained from it by fractional distillation: *Petroleum ether*, specific gravity 0.665–0.67, distilling about 50–60°, consists of pentane and hexane; petroleum benzine, not to be confounded with the benzene of coal tar, has a specific gravity of 0.68–0.72, distils at 70–90°, and is composed of hexane and heptane; ligroïne, boiling from 90°–120°, consists principally of heptane and octane; refined petroleum, called also kerosene, boils from 150–300° and has a specific gravity of 0.78–0.82. The portions boiling at higher temperatures are applied as lubricants; small amounts of vaseline and paraffins (see below) are obtained from them.

Caucasian petroleum (from Baku) has a higher specific gravity than the American; it contains far less of the light volatile constituents, and distils about 150°. Upwards of 10 per cent. benzene hydrocarbons (C_6H_6 to cymene $C_{10}H_{14}$) may be extracted by shaking it with concentrated sulphuric acid; and in addition less saturated hydrocarbons, C_nH_{2n-8}, etc., (*Ber.*, 19, Ref. 672). These latter are also present in the German oils (Naphthenes, *Ber.*, 20, 605). That portion of the Caucasian petroleum insoluble in sulphuric acid consists almost exclusively of C_nH_{2n} hydrocarbons, of peculiar constitution. They are designated naphthenes, octonaphthene, C_8H_{16}, nononaphthene, C_9H_{18} (*Ber.*, 16, 1873; 18, Ref. 186). At present they are considered identical with the benzene hexa-hydrides (octonaphthene is xylene-hexahydride, nononaphthene is mesitylene hexahydride (*Ber.*, 20, 1850, Ref. 570). From its composition, Gallician petroleum occupies a position intermediate between the American and that from Baku (*Annalen*, 220, 188).

German petroleum also contains benzene hydrocarbons (extracted by sulphuric acid), but consists chiefly of the saturated hydrocarbons and naphthenes (Kraemer, *Ber.*, 20, 545). The so-called petrolic acids are present in all varieties of petroleum (see oleic acids).

Products similar to those afforded by American petroleum, are yielded by the tar resulting from the dry distillation of cannel coal (in Scotland) and a variety of coal found in Saxony. The combustible oils obtained from the latter usually bear the names, *photogene* and *solar oil.* Large quantities of solid paraffins are also present in these tar oils.

By *paraffins*, we ordinarily understand the high-boiling (beyond 300°) solid hydrocarbons, arising from the distillation of the tar obtained from turf, lignite and bituminous shales. They are more abundant in the petroleum from Baku than in that from America. Mineral wax, ozokerite (in Gallicia and Roumania) and neftigil (in Baku), are examples existing in a free solid condition. For their purification, the crude paraffins are treated with concentrated sulphuric acid, to destroy the resinous constituents, and then re-distilled. Ozokerite that has been directly bleached, without distillation, bears the name *ceresine*, and is used as a substitute for beeswax. Paraffins that liquefy readily and fuse between 30–40°, are known as *vaselines;* they find application as salves.

When pure, the paraffins form a white, translucent, leafy, crystalline mass, soluble in ether and hot alcohol. They melt between 45° and 70°, and are essentially a mixture of hydrocarbons boiling above 300°, but appear to contain also those of the formula C_nH_{2n}. Chemically, paraffin is extremely stable, and is not attacked by fuming nitric acid. Substitution products are formed when chlorine acts upon paraffin in a molten state.

The hydrocarbons, $C_{22}H_{48}$, $C_{24}H_{30}$ and $C_{28}H_{58}$, were isolated from a commercial paraffin, melting at 52–54°, by fractional distillation and crystallization.

They have been proved identical with the normal paraffins prepared artificially (see p. 76).

Another paraffin, known as scaly paraffin, has been resolved into hydrocarbons ranging from heptdecane, $C_{17}H_{36}$, to $C_{23}H_{48}$ (tricosane), *Ber.*, **21**, 2256).

Caucasian ozokerite consists mainly of one hydrocarbon (called lekene) melting at 79°, and having the composition C_nH_{2n+2} or C_nH_{2n} (*Berichte*, **16**, 1548).

(2) UNSATURATED HYDROCARBONS C_nH_{2n}.

ALKYLENS OR OLEFINES.

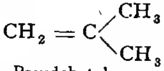
C_2H_4	Ethylene.	C_6H_{12}	Hexylene.
C_3H_6	Propylene.	C_7H_{14}	Heptylene.
C_4H_8	Butylene.	C_8H_{16}	Cetene.
C_5H_{10}	Amylene.	$C_{30}H_{60}$	Melene.

The hydrocarbons of this series contain two hydrogen atoms less than the first series. In their general structure, two adjacent carbon atoms are united by two affinity units each—by double linking (see p. 42):

$$\underset{\text{Ethylene.}}{CH_2 = CH_2} \qquad \underset{\text{Propylene.}}{CH_3—CH = CH_2}$$

Three structural cases are possible for the third member:—

$$(1)\ \underset{\text{Butylene.}}{CH_3—CH_2—CH = CH_2} \qquad (2)\ \underset{\text{Isobutylene.}}{CH_3—CH = CH—CH_3}$$

(3) 

$$CH_2 = C\begin{cases} CH_3 \\ CH_3 \end{cases}$$

Pseudobutylene.

Five isomerides of the formula C_5H_{10} are possible.* The most important general methods for the preparation of these hydrocarbons are:—

(1) Distil the monohydric alcohols, $C_nH_{2n+1}OH$, with dehydrating agents, *e. g.*, sulphuric acid, chloride of zinc, and phosphorus or boron trioxide. These remove one molecule of water:—

$$\underset{\text{Alcohol.}}{C_2H_6O} — H_2O = \underset{\text{Ethylene.}}{C_2H_4}$$

The secondary and tertiary alcohols decompose with special readiness. The higher alcohols, not volatile without decomposition, suffer the above change when heat is applied to them; thus cetene, $C_{16}H_{32}$, is formed on distilling cetyl alcohol, $C_{16}H_{34}O$.

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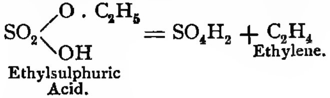
* The ring-shaped atomic linkings, exemplified in trimethylene, C_3H_6, and tetramethylene, C_4H_8 (see p. 42), are not included here. Their properties are different from those of the alkylens, and they at the same time form a transition to the closed ring of benzene. For this reason they will be considered after the fatty bodies.

When sulphuric acid acts upon the alcohols, acid esters of sulphuric acid (the so-called acid ethereal salts—see these) appear as intermediate products. When heated these break up into sulphuric acid and $C_n H_{2n}$ hydrocarbons :—

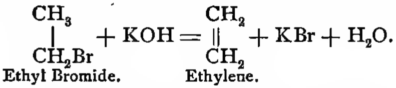


$$\underset{\text{Ethylsulphuric Acid.}}{SO_2\begin{cases} O \,.\, C_2H_5 \\ OH \end{cases}} = SO_4H_2 + \underset{\text{Ethylene.}}{C_2H_4}$$

The higher olefines may be obtained from the corresponding alcohols by distilling the esters they form with the fatty acids. The products are an olefine and an acid (*Berichte*, **16**, 3018) :—

$$\underset{\text{Dodecyl Ether of Palmitic Acid.}}{C_{16}H_{31}O \,.\, O \,.\, C_{12}H_{25}} = \underset{\text{Palmitic Acid.}}{C_{16}H_{31}O \,.\, OH} + \underset{\text{Dodecylene.}}{C_{12}H_{24}}$$

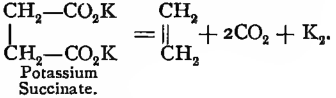
(2) The halogen derivatives, readily formed from the alcohols, are digested with alcoholic sodium or potassium hydroxide :—



$$\underset{\text{Ethyl Bromide.}}{\begin{matrix} CH_3 \\ | \\ CH_2Br \end{matrix}} + KOH = \underset{\text{Ethylene.}}{\begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix}} + KBr + H_2O.$$

In this reaction also, the haloid (especially the iodides) derivatives corresponding to the secondary and tertiary alcohols break up very readily. Heating with lead oxide effects the same result (*Berichte*, 11, 414).

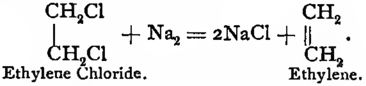
(3) Electrolyze the alkali salt of a dibasic acid (see p. 71) :—



$$\underset{\text{Potassium Succinate.}}{\begin{matrix} CH_2—CO_2K \\ | \\ CH_2—CO_2K \end{matrix}} = \begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix} + 2CO_2 + K_2.$$

This reaction is perfectly analogous to the formation of the dialkyls from the monobasic fatty acids (see p. 72).

(4) The olefines also result, on heating some of the dihalogen compounds, $C_nH_{2n}X_2$, with sodium :—



$$\underset{\text{Ethylene Chloride.}}{\begin{matrix} CH_2Cl \\ | \\ CH_2Cl \end{matrix}} + Na_2 = 2NaCl + \underset{\text{Ethylene.}}{\begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix}}.$$

The olefines can be prepared synthetically according to methods similar to those employed with the normal hydrocarbons (see p. 69).

The formation of higher alkylens in the action of lower members with tertiary alcohols or alkyl-iodides is noteworthy. Thus, from tertiary butyl alcohol and isobutylene, with the assistance of zinc chloride or sulphuric acid, we get isodibutylene, (*Annalen*, 189, 65) :—

$$(CH_3)_3C \,.\, OH + CH_2 : C(CH_3)_2 = \underset{\text{Isodibutylene.}}{(CH_3)_3C \,.\, CH : C(CH_3)_2} + H_2O.$$

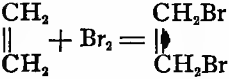
Tetramethyl ethylene (*Berichte*, 16, 398) is singularly produced on heating β-isoamylene (see p. 85) with methyl iodide and lead oxide:—

$$(CH_3)_2C : CH . CH_3 + CH_3I = (CH_3)_2C : C(CH_3)_2 + HI.$$

In the dry distillation of many complicated carbon compounds, the olefines are produced along with the normal paraffins, hence their presence in illuminating gas and in tar oils.

As far as physical properties are concerned the olefines resemble the normal hydrocarbons; the lower members are gases, the intermediate ethereal liquids, while the higher (from $C_{16}H_{32}$ up) are solids. Generally their boiling points are a few degrees higher than those of the corresponding paraffins.

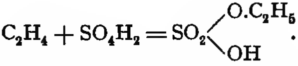
Being unsaturated, they can unite directly with two univalent atoms or groups; then the double binding becomes single. With chlorine, bromine and iodine they combine directly:



$$\begin{array}{l}CH_2\\ \|\\ CH_2\end{array} + Br_2 = \begin{array}{l}CH_2Br\\ |\\ CH_2Br\end{array}$$

, forming oily liquids; hence the designation of ethylene as olefiant gas, and that of *olefines* for the entire series. The liquid olefines react very energetically with bromine; on this account they should be cooled and diluted with ether.

Concentrated sulphuric acid absorbs them, forming ethereal salts:—

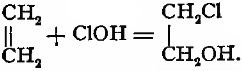


$$C_2H_4 + SO_4H_2 = SO_2\begin{array}{l}\diagup O.C_2H_5\\ \diagdown OH\end{array}.$$

Very often the absorption takes place only at high temperatures.

They combine, too, directly with HCl, HBr and with especial readiness with HI.

They yield so-called chlorhydrins with aqueous hypochlorous acid:—



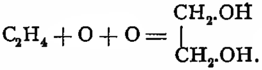
$$\begin{array}{l}CH_2\\ \|\\ CH_2\end{array} + ClOH = \begin{array}{l}CH_2Cl\\ |\\ CH_2OH.\end{array}$$

Nascent hydrogen (zinc and hydrochloric acid, or sodium amalgam) converts the olefines into the saturated hydrocarbons: $C_2H_4 + H_2 = C_2H_6$.

Concentrated hydriodic acid effects the same if aided by heat, and, especially, when phosphorus is present. The iodide formed at first is reduced by a second molecule of HI:—

$$C_2H_4 + HI = C_2H_5I \text{ and}$$
$$C_2H_5I + HI = C_2H_6 + I_2.$$

Oxidation of Olefines. It has been generally supposed that when the olefines were exposed to the action of oxidizing agents (*e. g.*, potassium permanganate, and chromic acid), they were split up at the point of their double union (*Ann.*, 197, 225). The most recent research, however, has demonstrated that two hydroxyl groups always result, thus giving rise to the formation of dihydric alcohols (see these) (Wagner, *Ber.*, 21, 1230 and 3359):—



$$C_2H_4 + O + O = \begin{array}{l} CH_2.OH \\ | \\ CH_2.OH. \end{array}$$

The unsaturated alcohols and acids are similarly oxidized. Potassium permanganate is without action upon trimethylene.

Polymerization of Olefines. When acted upon by dilute hydrochloric acid, zinc chloride, boron fluoride and other substances, many olefines sustain, even at ordinary temperatures, a polymerization, in consequence of the union of several molecules. Thus there result from isoamylene, C_5H_{10}: di-isoamylene, $C_{10}H_{20}$; tri-isoamylene, $C_{15}H_{30}$, etc., etc. Butylene and propylene behave in the same way. Ethylene, on the other hand, is neither condensed by sulphuric acid nor by boron fluoride. The polymerides act like unsaturated compounds, and are capable of binding two affinities.

The nature of the binding of the carbon atoms in polymerization is, in all probability, influenced by the different structure of the alkylens. The manner of formation and structure of the isodibutylene produced from isobutylene correspond to the formulas:—

$$\underset{\text{2 Mols. Isobutylene.}}{(CH_3)_2C : CH_2 + CH_2 : C(CH_3)_2} = \underset{\text{Isodibutylene.}}{(CH_3)_3C.CH : C(CH_3)_2.}$$

Tertiary butyl alcohol very probably figures as an intermediate product, and afterwards unites with a second molecule of isobutylene, and condenses to isodibutylene.

Although ethylene suffers no alteration, yet its substitution products polymerize very readily.

Methylene, CH_2, the first member of the series $C_n H_{2n}$, does not exist. In all the reactions in which it might be expected to occur, for instance, when copper acts on methylene iodide, $CH_2 I_2$, we obtain only polymerides; ethylene, C_2H_4, propylene, C_3H_6, etc.

(1) **Ethylene,** C_2H_4 (olefiant gas), is formed in the dry distillation of many organic substances, and is, therefore, present in illuminating gas (6 per cent.). It is best prepared by the action of sulphuric acid upon ethyl alcohol.

A mixture of 1 vol. 80 per cent. alcohol and 6 vols. sulphuric acid is permitted to stand for awhile, then heated, in a capacious vessel, upon a sand bath. The foaming may be prevented by the addition of sand. The liberated gas is conducted through a vessel containing potassium hydroxide, to remove CO_2 and SO_2, and, finally, collected over water (*Annalen*, 192, 244).

Ethylene is a colorless gas, with a peculiar, sweetish odor. Its sp. gr. equals 14 ($H = 1$). Water dissolves but small quantities of it, while alcohol and ether absorb about 2 volumes. It is liquefied at 0°, and a pressure of 42 atmospheres. At ordinary pressure it boils at —105°, and is suitable for the production of very low temperatures. It burns with a bright, luminous flame, decomposing into CH_4 and C. In chlorine gas the flame is very smoky; a mixture of ethylene and chlorine burns away slowly when ignited. It forms a very explosive mixture with oxygen (3 volumes).

When in alcoholic solution ethylene combines readily with chlorine, bromine and iodine. Fuming hydriodic acid absorbs it with formation of C_2H_5I. Aided by platinum black it will combine with H_2 at ordinary temperatures, yielding C_2H_6. At the ordinary temperature it combines with sulphuric acid only after continued shaking; the absorption is, however, rapid and complete at 160–174°. By boiling the resulting ethylsulphuric acid with water we can get alcohol. Potassium permanganate oxidizes ethylene first to ethylene glycol, $C_2H_4(OH)_2$ (p. 82), and then to oxalic and formic acids.

(2) **Propylene,** $C_3H_6 = CH_3.CH : CH_2$, is obtained from many organic substances, *e. g.*, amyl alcohol, when their vapors are conducted through red-hot tubes. Propyl and isopropyl iodide are converted into it when boiled with alcoholic potash:—

$$C_3H_7I + KOH = C_3H_6 + KI + H_2O.$$

The same end is achieved by the action of nascent hydrogen (zinc and hydrochloric acid) or hydriodic acid upon allyl iodide:—

$$C_3H_5I + HI = C_3H_6 + I_2.$$

Preparation.—1. Digest a mixture of 80 gr. isopropyl iodide, 50 gr., 95 per cent. alcohol, and 50 gr. KOH upon a water bath; at 40–50° a regular stream of propylene escapes. 2. A solution of allyl iodide in glacial acetic acid, or, better, one in alcohol, is allowed to drop upon granulated zinc (*Ber.*, 6, 1550).

Propylene is a gas, liquefiable under great pressure. It combines directly with the halogens and their hydrides. Concentrated H_2SO_4 dissolves it with formation of isopropyl sulphuric acid and polymeric propylenes $(C_3H_6)_n$. It dissolves in concentrated HI, yielding isopropyl iodide:—

$$CH_3 - CH = CH_2 + HI = CH_3 - CHI - CH_3.$$

Trimethylene, C_3H_6, isomeric with propylene, is obtained from trimethylene bromide (see p. 102), by aid of sodium. Unlike propylene, it unites with difficulty with bromine to trimethylene bromide, and with HI to normal propyl iodide. It appears to contain a closed carbon chain (see p. 42), and, with its derivatives, is considered after the fatty bodies.

(3) **Butylenes**, C_4H_8.—Theoretically, three isomerides are possible:—

$CH_3 . CH_2 . CH : CH_2$ — α-Butylene $CH_3 . CH : CH . CH_3$ — β-Butylene $(CH_3)_2C : CH_2$. — Isobutylene.

(1) *α-Butylene* (normal Butylene) is formed from normal butyl iodide, $CH_3 . CH_2 . CH_2 . CH_2I$, by aid of alcoholic potash; and also from bromethylene and zinc-ethyl: $2CH_2 : CHBr + (C_2H_5)_2Zn = 2CH_2 : CH . C_2H_5 + ZnBr_2$. In the cold it condenses to a liquid, boiling at —5°. With HI, it forms secondary butyl iodide, $CH_3 \ \ CH_2 . CHI . CH_3$. Its bromide, $C_4H_8Br_2$, boils at 66°.

(2) *β-Butylene* (pseudo-butylene) results from secondary butyl iodide (see above) and alcoholic potash or mercuric cyanide; also (together with isobutylene) from isobutyl alcohol, in which case there occurs a molecular transposition. It boils at + 1° and solidifies on cooling. It yields secondary butyl iodide with HI. Its bromide, $C_4H_8Br_2$, boils at 159°, and is changed by alcoholic potash to crotonylene, $CH_3 . C : C . CH_3$ (p. 89). See *Ann.*, 250, 252, for the geometrical isomerides of pseudobutylene.

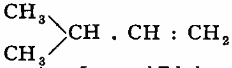
(3) *Isobutylene* is obtained from isobutyl iodide, $(CH_3)_2 CH . CH_2I$, and tertiary butyl iodide, $(CH_3)_2CI . CH_3$, when alcoholic potash acts upon them; further from isobutyl alcohol, $(CH_3)_2 . CH . CH_2OH$, when heated with zinc chloride or sulphuric acid. Pseudo-butylene appears at the same time (*Berichte*, 13, 2395 and 2404, 16, 2284). For a method of separating these two butylenes, consult *Ber.*, 19, Ref. 554. It boils at — 6° and dissolves in sulphuric acid (diluted one half with water), forming butyl-sulphuric acid. The latter yields trimethyl carbinol, when boiled with water. Concentrated HI absorbs isobutylene with formation of tertiary butyl iodide. Its *bromide* boils at 149°. Potassium permanganate oxidizes isobutylene to its glycol, $(CH_3)_2 . C(OH) . CH_2(OH)$ (p. 82).

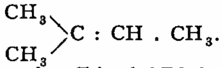
When isobutylene is digested with H_2SO_4 and H_2O (equal volumes) it becomes isodibutylene, $(CH_3)_3C . CH : C(CH_3)_2$, boiling at 130° (see p. 81).

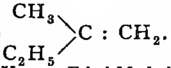
(4) **Amylenes**, C_5H_{10}.—Five isomerides are theoretically possible:—

(1) $CH_3 . CH_2 . CH_2 . CH : CH_2$.
α-Amylene, Normal Propyl Ethylene.

(2) $CH_3 . CH_2 . CH : CH . CH_3$.
β-Amylene, Ethyl Methyl Ethylene.

(3)

$\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right\rangle CH . CH : CH_2$
α-Isoamylene, Isopropyl Ethylene.

(4)

$\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right\rangle C : CH . CH_3$.
β-Isoamylene, Trimethyl Ethylene.

(5)

$\left.\begin{matrix}CH_3\\C_2H_5\end{matrix}\right\rangle C : CH_2$.
γ-Amylene, Unsym. Ethyl Methylethylene.

(1) *α-Amylene*, $C_3H_7 . CH : CH_2$ (normal amylene, propylethylene), has not yet been prepared in a pure condition; it appears to be that part of ordinary amylene (see below) which is insoluble in sulphuric acid, boils about 37° and is oxidized by a $KMnO_4$ solution chiefly to butyric and formic acids (*Annalen*, 197, 253). It unites with HI to the iodide, $C_3H_7 . CHI . CH_3$, boiling at 144°.

(2) *β Amylene*, $C_2H_5 . CH : CH . CH_3$ (sym. ethylmethyl-ethylene), is produced from the iodide of diethylcarbinol, $C_2H_5 . CHI . C_2H_5$, boiling at 145°. The boiling point of β-amylene is 36°; with HI it yields the same iodide as α-amylene. Its bromide, $C_5H_{10}Br_2$, boils at 178°.

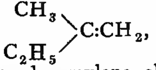
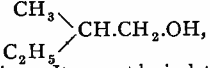
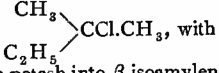
(3) *α-Isoamylene*, $(CH_3)_2CH.CH:CH_2$ (isopropyl ethylene), is formed together with γ-amylene, from the iodide of the amyl alcohol of fermentation (see this), by the action of alcoholic potash (*Annalen*, 190, 351). A mixture of these two

amylenes results, and boils at 23–27°. On shaking with cold H_2SO_4 (diluted one-half with water) the γ-variety dissolves, leaving α-isoamylene unaltered (about 60 per cent. of the mixture). Similarly, by action of HI (or HBr) upon the mixture at —20°, γ-amylene is changed to the iodide, while α-amylene is not affected. It yields propyl-ethylene glycol when oxidized with potassium permanganate. Isoamylene boils at 21.1°–21.3°. It does not unite in the cold (below 0°) with H_2SO_4, HI, or HBr. At ordinary temperatures it combines gradually with HI, HBr, and HCl, yielding derivatives of methyl isopropyl carbinol, $(CH_3)_2.CH.CHX.CH_3$.

(4) *β-Isoamylene,* $(CH_3)_2.C{:}CH.CH_3$ (trimethyl ethylene) produced from the iodides of methyl isopropyl carbinol, $(CH_3)_2CH.CHI.CH_3$, and dimethyl-ethyl carbinol, $(CH_3)_2.CI.CH_2.CH_3$, boils at 36–38°. At ordinary temperatures it reunites with HI to the iodide, $(CH_3)_2.CI.CH_2.CH_3$. It combines readily, in the cold, with sulphuric acid to the sulphuric ether, and the latter, when boiled with water, affords dimethyl-ethyl carbinol, $(CH_3)_2.C(OH).CH_2CH_3$.

β-Isoamylene is the chief ingredient of the ordinary amylene obtained from fermentation amyl alcohol by distillation with zinc chloride. (See *Annalen*, 190, 332.) The product, boiling about 25–40°, is a mixture of β-isoamylene (50 per cent.) with pentane (boiling about 29°) and probably contains, in addition, γ-amylene and also α-amylene. On shaking crude amylene in the cold (—20°) with sulphuric acid, diluted with ½-1 vol. of H_2O, the β-isoamylene dissolves (also any γ-amylene that may be present) to amyl-sulphate, which yields dimethyl-ethyl carbinol, $(CH_3)_2.C(OH).CH_2.CH_3$. The chief constituents of the undissolved oil are pentane and α-amylene, which are oxidized by $KMnO_4$ to butyric and formic acids (see above).

On shaking ordinary crude amylene with H_2SO_4 (diluted with ½ vol. water), without cooling, polymeric amylenes are produced: diamylene, $C_{10}H_{20}$, boiling at 156°, triamylene, $C_{15}H_{30}$, boiling at 240–250°, and tetramylene, boiling about 360°. All these are oily liquids, which combine with bromine.

(5) *γ-Amylene,*  $\begin{matrix}CH_3\\C_2H_5\end{matrix}\!\!>\!C{:}CH_2$, (unsym. methyl-ethyl ethylene), is contained (40 per cent.) in crude amylene, obtained from the iodide of fermentation amyl alcohol (see above 3), hence, very probably also present in ordinary amylene. It very likely comes from the active alcohol,  $\begin{matrix}CH_3\\C_2H_5\end{matrix}\!\!>\!CH.CH_2.OH$, present in the fermentation alcohol, although itself not active. It cannot be isolated because of its very ready union with H_2SO_4 and HI, even in the cold. Both the sulphuric acid ether from it and the iodide yield tertiary amyl alcohol. The iodide of active amyl alcohol furnishes an amylene boiling at 31° (Le Bel). This is probably pure γ-amylene. It gives the chloride,  $\begin{matrix}CH_3\\C_2H_5\end{matrix}\!\!>\!CCl.CH_3$, with HCl. This boils at 87°, and decomposes with alcoholic potash into β-isoamylene.

Various higher olefines have been prepared from the corresponding alcohols. The highest can be made by the distillation of the esters derived from the alcohols and the higher fatty acids (p. 80). In this way the following olefines of normal structure have been prepared:

		Melting Point.	B. P. at 15 mm.	Sp. Gr.
Dodecylene	$C_{12}H_{24}$	—31.5°	96°	0.7954
Tetradecylene	$C_{14}H_{28}$	—12°	127°	0.7936
Hexadecylene	$C_{16}H_{32}$	+4°	154°	0.7917
Octodecylene.............	$C_{16}H_{36}$	+18°	179°	0.7910

Hexadecylene, $C_{16}H_{32}$, is sometimes called *cetene;* it was first obtained from cetyl alcohol, and at ordinary temperatures boils about 240°. Cerotene, from Chinese wax, melts at 58°, while melene, $C_{30}H_{60}$, from ordinary wax, melts at 62°.

(3) HYDROCARBONS C_nH_{2n-2}.

ACETYLENE SERIES.

C_2H_2	Acetylene.	C_5H_8	Valerylene.
C_3H_4	Allylene.	C_6H_{10}	Hexoylene.
C_4H_6	Crotonylene.		

The above hydrocarbons, differing from the normal C_nH_{2n+2} by four atoms of hydrogen, may be based upon two structurally different but possible formulas. In one case we assume a triple union of two neighboring carbon atoms—

$$\underset{\text{Acetylene.}}{CH{\equiv}CH} \qquad \underset{\text{Allylene.}}{CH_3{-}C{\equiv}CH}$$

while in the second a double union occurs twice—

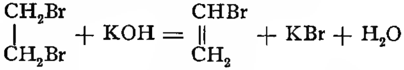
$$\underset{\text{Isomeric Allylene.}}{CH_2 = C = CH_2} \qquad \underset{\text{Diallyl.}}{CH_2 = CH{-}CH_2{-}CH_2{-}CH = CH_2.}$$

This structural difference is abundantly manifest in the varying chemical behavior, since only members of the first class (having the group $\equiv CH$) that can be regarded as true acetylenes, possess the power of entering into combination with copper and silver, thereby yielding derivatives in which the H of the group $\equiv CH$ is replaced by metals.

These compounds result from the action of acetylene upon ammoniacal silver nitrate and cupric chloride solutions (p. 87). The silver derivatives are obtained without difficulty by using an alcoholic solution of silver nitrate (*Ber.*, 21, Ref. 609).

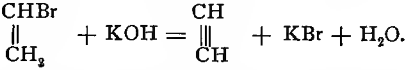
Diolefines, such as diallyl (see above), do not form copper and silver compounds, but produce precipitates with mercury sulphate and chloride in aqueous solution (*Ber.*, 21, Ref. 185 and 717, and allylene, p. 89).

The hydrocarbons of this series are produced according to the same methods as those of the ethylene series. They are formed on heating the haloids, $C_nH_{2n-1}X$ (corresponding to the alcohols of the allyl series) and $C_nH_{2n}X_2$, with alcoholic potash; in the latter case the reaction proceeds in two phases—



$$\begin{matrix} CH_2Br \\ | \\ CH_2Br \end{matrix} + KOH = \begin{matrix} CHBr \\ \| \\ CH_2 \end{matrix} + KBr + H_2O$$

and

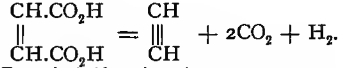


$$\begin{matrix} CHBr \\ \| \\ CH_2 \end{matrix} + KOH = \begin{matrix} CH \\ \text{|||} \\ CH \end{matrix} + KBr + H_2O.$$

If the heating with alcoholic potash be too violent the acetylene which has formed frequently sustains a *transposition;* thus, ethyl acetylene, $C_2H_5.C\equiv CH$, yields dimethyl acetylene, $CH_3.C\equiv C.CH_3$, and propyl acetylene, $C_3H_7.C\equiv CH$, furnishes ethyl methyl acetylene, $C_2H_5.C\equiv C.CH_3$, etc. (*Ber.*, 20, Ref. 781).

The reverse transposition sometimes occurs on heating with metallic sodium: ethyl methyl acetylene passes into propyl acetylene, and dimethyl allene, $(CH_3)_2C=C=CH_2$, yields isopropyl acetylene, etc. (*Ber.*, 21, Ref. 177).

Acetylenes also arise in the electrolysis of unsaturated dibasic acids (compare p. 80).



$$\begin{matrix} CH.CO_2H \\ \| \\ CH.CO_2H \end{matrix} = \begin{matrix} CH \\ \text{|||} \\ CH \end{matrix} + 2CO_2 + H_2.$$

Fumaric Acid. Acetylene.

As unsaturated compounds of second degree, the hydrocarbons C_nH_{2n-2} are capable of adding to themselves four affinity units. Hence they unite with one and two molecules of the halogens and their hydrides. Thus acetylene forms $C_2H_2Br_2$ and $C_2H_2Br_4$. They are absorbed by concentrated sulphuric acid with the formation of sulphuric ethers; condensation occurs at the same time. Nascent hydrogen converts them into the hydrocarbons C_nH_{2n} and C_nH_{2n+2}.

In the presence of $HgBr_2$ and other salts of mercury, the acetylenes can unite with water. In this way we get from acetylene, aldehyde, C_2H_4O, from allylene, C_3H_4, acetone, C_3H_6O, from valerylene, C_5H_8, a ketone, $C_5H_{10}O$ (*Berichte*, 14, 1542 and 17, 28). Very often moderately dilute sulphuric acid will act in the same way (see Allylene).

A characteristic of the true acetylenes is their power to yield solid crystalline compounds by the action of ammoniacal solutions of silver and copper salts. Hydrochloric acid will again liberate the acetylenes from these salts. This behavior affords a very convenient method for separating the acetylenes from other gases, as well as obtaining them in a pure condition.

Like the alkylens (p. 82) the acetylenes condense, and in this manner we very frequently obtain bodies that belong to the benzene series. At a red heat benzene, C_6H_6, is obtained from acetylene, C_2H_2; mesitylene, C_9H_{12} (trimethylbenzene, $C_6H_3(CH_3)_3$), from allylene, C_3H_4, by the action of sulphuric acid, and hexamethyl benzene, $C_{12}H_{18}$ (see p. 89), from crotonylene, C_4H_6.

Acetylene, C_2H_2, is formed when many carbon compounds, like alcohol, ether, marsh gas, methylene, etc., are exposed to intense heat (their vapors conducted through tubes heated to redness). Hence it is present in illuminating gas, to which it imparts a peculiar odor. Its direct synthesis from carbon and hydrogen is described on p. 70; acetylene results, too, in the decomposition of calcium carbide by water. Its formation in the electrolysis of the alkali salts of fumaric and maleic acids is significant:—

$$C_2H_2(CO_2H)_2 = C_2H_2 + 2CO_2 + H_2.$$

It is produced when silver, copper or zinc dust acts upon iodoform.

Preparation.—1. Ethylene bromide, $C_2H_4Br_2$, is heated with two parts of KOH and strong alcohol, in a flask provided with an upright condenser. The escaping gas is conducted through an ammoniacal silver solution, the precipitate washed with water and decomposed by hydrochloric acid (*Annalen*, 191, 368). 2. Let the flame of a Bunsen burner strike back, *i. e.*, burn within the tube, and then aspirate the gases through a silver solution (Berthelot's apparatus).

Acetylene is a gas of peculiar, penetrating odor, and may be liquefied at + 1° and under a pressure of 48 atmospheres. It is slightly soluble in water; more readily in alcohol and ether. It burns with a very smoky flame. The color of the copper compound, $C_2HCu.CuOH$, is red, while that of the silver derivative, $C_2HAg.AgOH$, is white; their composition is not definitely established. When heated, both explode very violently. When acetylene is conducted through ammoniacal silver chloride, a white, curdy precipitate, $C_2HAg.AgCl$, is thrown out of solution. Sodium heated in acetylene gas disengages hydrogen, and we obtain the compounds C_2HNa and C_2Na_2.

Nascent hydrogen (zinc and ammonia) converts acetylene into C_2H_4 and C_2H_6; and when hydrogen and acetylene are passed over platinum black, C_2H_6, is formed.

Acetylene reacts very energetically with chlorine gas. It forms a crystalline compound with $SbCl_5$, but heat changes this to dichlor-ethylene, CHCl : CHCl and $SbCl_3$. With bromine it forms $C_2H_2Br_2$ and $C_2H_2Br_4$.

Monochlor-acetylene, C_2HCl, obtained from dichloracrylic acid, is an explosive gas.

Monobrom-acetylene, C_2HBr, obtained by boiling acetylene dibromide with alcoholic potash, is a gas that inflames in contact with air. Below 0° it condenses to a liquid, which on exposure to the light polymerizes to a yellow powder. The latter contains symmetrical tri-brom-benzene, $C_6H_3Br_3$.

Mono-iodo-acetylene, C_2HI, results on boiling iodopropargylate of barium with water. It is an oil with a very disagreeable odor. It solidifies on cooling. When preserved it polymerizes to tri-iodo-benzene, $C_6H_3I_3$ (*Ber.*, 18, 2274).

Di-iodo-acetylene, C_2I_2, results from the action of iodine upon the silver compound of acetylene. It melts at 78°. It is very readily decomposed when exposed to a higher heat. In the light it polymerizes to hexa-iodo-benzene, C_6I_6.

Allylene, $C_3H_4 = CH_3—C{\equiv}CH$. This is produced by the action of alcoholic potash upon monochlor-propylene, $CH_3.CCl:CH_2$, and by heating dichloracetone chloride, $CH_3.CCl_2.CHCl_2$, with sodium; further, in the electrolysis of the alkali salts of mesaconic and citraconic acids. It is very similar to acetylene. Its copper compound is siskin green in color; the silver derivative, C_3H_3Ag, is white. Allylene forms the compound $(C_3H_3)_2Hg$ with mercuric oxide. This crystallizes from alcohol in brilliant needles; acids decompose it into allylene and a mercury salt. With bromine we get the liquid bromides, $C_3H_4Br_2$ and $C_3H_4Br_4$; and with two molecules of the halogen hydrides the compounds $CH_3.CX_2.CH_3$.

Allylene is soluble in concentrated sulphuric acid. A large quantity of acetone is produced by diluting this solution with water; but on distilling it the allylene condenses to mesitylene: $3C_3H_4 = C_9H_{12}$, a benzene derivative. In the presence of mercury salts, allylene combines with water to form acetone (see p. 87).

Isomeric Allylene, $CH_2:C:CH_2$. This does not unite with copper and silver. It is produced by the electrolysis of potassium itaconate; by the action of sodium upon dichlor-propylene, $C_3H_4Cl_2$ (from dichlorhydrin, see glycerol), or of zinc dust and alcohol upon dibrom-propylene, $C_3H_4Br_2$ (from tribromhydrin) (*Ber.*, 21, Ref. 717). It forms precipitates in aqueous solutions of mercuric sulphate or chloride (p. 86). Sulphuric acid and water convert it into acetone, and when, heated with sodium to 100° it passes into allylene. With bromine it forms a tetrabromide, $C_3H_4Br_4$, crystallizing in leaflets and melting at 195°.

Crotonylene, C_4H_6, Valerylene, C_5H_8, Hexoylene, C_6H_{10}, or Butine, Pentine Hexine, etc., are the higher members of the series C_nH_{2n-2}.

Crotonylene, $CH_3.C{\vdots}C.CH_3$—dimethyl acetylene (*Ann.*, 250, 252), is a strong smelling liquid obtained from the bromide of pseudo-butylene, $CH_3.CH:CH.CH_3$, by the action of alcoholic potash. Its boiling point is 180°. When it is shaken with sulphuric acid (diluted ⅓ with water), it is converted into solid hexamethyl benzene, $C_6(CH_3)_6$, melting at 164°:—

$$3C_4H_6 = C_{12}H_{16} = C_6(CH_3)_6.$$

Diallyl, $CH_2:CH.CH_2.CH_2.CH:CH_2$, is produced when silver or sodium acts upon allyl iodide (see p. 98), and by distilling allyl mercury iodide, C_3H_5HgI, with potassium cyanide. It boils at 59°, and when oxidized with $KMnO_4$ yields two isomeric diglycols, $C_6H_{10}(OH)_4$ (*Ber.*, 21, 3344). It forms two tetrabromides, $C_6H_{10}Br_4$, the crystalline melting at 63°, and the other a liquid (*Ber.*, 22, 2497). As it does not contain the group $\equiv CH$, it forms no metal derivatives. Higher members have been obtained from the dibromides of the higher alkylens (p. 86), *Ber.*, 17, 1374:—

		M. P.	B. P. at 15 mm.	sp. gr.
Dodecylidene, ...	$C_{12}H_{22}$	—9°	105°	0.8097
Tetradecylidene, ...	$C_{14}H_{26}$	+6.5°	134°	0.8064
Hexadecylidene, ...	$C_{18}H_{30}$	20°	160°	0.8039
Octadecylidene, ...	$C_{18}H_{34}$	30°	184°	0.8016

(4) HYDROCARBONS $C_n H_{2n-4}$.

Various bodies of this series have been obtained from the tar oil (from cannel coal) boiling as high as 300°. In all probability they result from the polymerization of the hydrocarbons $C_n H_{2n-2}$, contained in the coal tar, through the agency of sulphuric acid.

The lowest member of this series would be vinyl acetylene, $C_4H_4 = CH_2$:CH.C ⋮ CH. It has not been isolated. Its homologue is

Valylene, C_5H_6, with the structure CH_3.CH:CH.C ⋮ CH or CH_2:C (CH_3). C ⋮ CH. This is obtained from valerylene dibromide, C_5H_8Br, by the action of alcoholic potassium hydroxide. It boils at 50°, and has an alliaceous odor. It forms precipitates with ammoniacal copper and silver solutions, and yields the hexabromide $C_5H_6Br_6$, with 6 atoms of bromine.

The terpenes, $C_{10}H_{16}$, are hydrogen addition products of benzene compounds, and are homologues of the hydrocarbons just described.

(5) HYDROCARBONS $C_n H_{2n-6}$

Diacetylene, C_4H_2 = HC ⋮ C.C ⋮ CH, is formed from diacetylene dicarbonic acid on heating its copper salt with potassium cyanide. It is a gas that yields a yellow precipitate with an ammoniacal silver solution. Iodine converts the silver compound into di-iodo-diacetylene, C_4I_2, a colorless, crystalline body, melting at 101°. It has an odor like that of iodoform. It explodes when heated.

Dipropargyl, C_6H_6 = CH ⋮ C.CH_2.CH_2.C ⋮ CH. This is isomeric with benzene, but its properties are entirely different. On warming solid crystalline diallyltetrabromide, $C_6H_{10}Br_4$ (see above), with KOH, there is formed dibrom-diallyl, $C_6H_8Br_2$ (together with a little dipropargyl), a liquid boiling at 205–210°. On treating the latter compound with alcoholic potash we obtain dipropargyl, C_6H_6. This is a very mobile liquid, of penetrating odor, and boiling at 85°; its specific gravity at 18° equals 0.81.

The compound $C_6H_4Cu_2 + 2H_2O$, which it forms with ammoniacal copper solutions is siskin yellow in color; that with silver, $C_6H_4Ag_2 + 2H_2O$, is white, but blackens on exposure to the air. Acids again liberate dipropargyl from these.

If dipropargyl be allowed to stand, or if heat be applied to it, it polymerizes and becomes thick and resinous. It unites energetically with bromine to $C_6H_6Br_4$ and $C_6H_6Br_8$; the latter melts at 140°.

Dimethyl Di-acetylene, CH_6.C≡C.C≡C.CH_3, is the second isomeride of benzene. It has been obtained from the copper derivative of allylene, CH_3.C—C.Me. It melts at 64° and boils at 130° (*Ber.*, 20, 564).

HALOGEN DERIVATIVES OF THE HYDROCARBONS.

The halogen substitution products result from the replacement of hydrogen in the hydrocarbons by the halogens. In general character they resemble the compounds from which they have their origin.

The following are the most important methods for their preparation:—

(1) By direct action of the halogens upon the hydrocarbons, when one or all the hydrogen atoms will suffer replacement, the hydrides of the halogens forming at the same time:—

$$C_n H_m + xCl_2 = C_n H_{m-x} Cl_x + xHCl.$$

The action of chlorine is accelerated, and very often also dependent upon direct sunlight, or the presence of small quantities of iodine. It is the ICl_3, which arises in the latter case, that facilitates the reaction. $SbCl_5$ also plays the rôle of a chlorine carrier, since upon heating it yields $SbCl_3$ and 2Cl. Ferric chloride serves as an excellent chlorine and bromine carrier (*Ann.*, 225, 196 and 231, 132). When the chlorination is very energetic a rupture of the carbon linking takes place (*Berichte*, 8, 1296, 10, 801). Heat hastens the action of bromine. Usually iodine does not replace well, inasmuch as the final iodine products sustain reduction through the hydriodic acid formed simultaneously with them:—

$$C_3H_7I + HI = C_3H_8 + I_2.$$

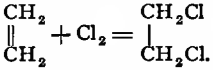
In the presence of substances (like HIO_3 and HgO) capable of uniting or decomposing HI, iodine frequently effects substitution:—

$$5C_3H_8 + 2I_2 + IO_3H = 5C_3H_7I + 3H_2O,$$
$$2C_3H_8 + 2I_2 + HgO = 2C_3H_7I + H_2O + HgI_2.$$

And in the presence of ferric chloride iodation occurs with the liberation of hydrogen chloride (*Ann.*, 231, 195).

In direct substitution a mixture of mono- and poly-substitution products generally results, and these are separated by fractional distillation or crystallization.

(2) By adding halogens to the unsaturated hydrocarbons:—



$$\begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix} + Cl_2 = \begin{matrix} CH_2Cl \\ | \\ CH_2Cl. \end{matrix}$$

At ordinary temperatures, chlorine and bromine react very violently; in the absence of light the action is more regular, and when it is present, substitution products also arise. Iodine (in alcoholic solution) generally enters combination only upon application of heat.

(3) By adding halogen hydrides to the unsaturated hydrocarbons. In concentrated aqueous solution, HI reacts very readily:—

$$CH_3.CH:CH_2 + HI = CH_3.CHI.CH_3.$$

Here again we observe the common rule that the halogen atom almost invariably attaches itself to the least hydrogenized carbon atom (*Annalen*, 179, 296 and 325). Sulphuric acid attaches itself similarly (p. 81). The reaction proceeds in accordance with the principle of the greatest heat evolution (*Ber.*, 21, Ref. 179).

(4) By replacing the hydroxyl groups of the alcohols $C_n H_{2n+1} OH$ by halogens. This is the most convenient method of preparing the

mono-halogen products, as the alcohols are very readily obtained. The transposition is brought about by heating the alcohol previously saturated with the halogen hydride:—

$$C_2H_5.OH + H\,Br = C_2H_5Br + H_2O.$$

This rearrangement between the two reacting compounds is, however, not complete. It depends very much on the mass of the substances reacting, and upon the temperature (compare esters of mineral and fatty acids). The alteration is most speedy with HI; however, transpositions sometimes occur in this case, in the higher alcohols. See p. 95.

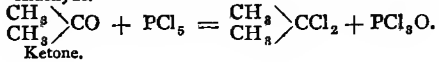
The change is most complete when effected by the halogen products of phosphorus:—

$$\begin{aligned} C_2H_5.OH + PCl_5 &= C_2H_5Cl + PCl_3O + HCl, \\ 3C_2H_5.OH + PCl_3O &= 3C_2H_5Cl + PO(OH)_3, \\ 3C_2H_5.OH + PCl_3 &= 3C_2H_5Cl + PO_3H_3. \end{aligned}$$

Even here the reaction is not perfect. Phosphoric and phosphorous acids are formed, and these convert a portion of the alcohol into ethereal salts, which constitute the residue after distilling off the halogen derivatives.

(5) By the action of PCl_5 and PBr_5 upon the aldehydes and ketones, when an atom of oxygen is replaced by two halogen atoms:—

$$\underset{\text{Aldehyde.}}{CH_3CHO} + PCl_5 = CH_3.CHCl_2 + PCl_3O,$$



$$\underset{\text{Ketone.}}{\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!CO} + PCl_5 = \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!CCl_2 + PCl_3O.$$

The halogen derivatives prepared according to these methods are partly identical, as will be seen further on, and partly isomeric. They are generally colorless, ethereal smelling liquids, *insoluble* in water. The iodides redden in sunlight, iodine separating. The chlorides and bromides burn with a green-edged flame.

Nascent hydrogen (zinc and hydrochloric acid or glacial acetic acid, sodium amalgam and water) can reconvert all the halogen derivatives, by successive removal of the halogen atoms, into the corresponding hydrocarbons:—

$$CHCl_3 + 3H_2 = CH_4 + 3HCl.$$

When the mono-halogen compounds are heated with moist silver oxide, the corresponding alcohols are produced:—

$$C_2H_5I + AgOH = C_2H_5.OH + AgI.$$

Alcoholic sodium and potassium hydroxides occasion the splitting off of a halogen hydride, and the production of unsaturated compounds: (pp. 80, 87):—

$$\underset{\text{Propyl Bromide.}}{CH_3.CH_2.CH_2Br} + KOH = \underset{\text{Propylene.}}{CH_3.CH{:}CH_2} + KBr + H_2O.$$

In this reaction the halogen attracts to itself the hydrogen of the least hydrogenized adjacent carbon atom (compare p. 91). Such a splitting sometimes occurs on application of heat, and it appears that the primary alkylogens are more easily decomposed than the secondary and tertiary (see p. 94).

(1) HALOGEN COMPOUNDS—$C_nH_{2n+1}X$.

ALKYLOGENS.

Because of their formation from the alcohols by the action of the halogen hydrides, the alkylogens are called *haloid esters*. They are perfectly analogous to the true esters produced by the action of alcohols and oxygen acids.

Monochlormethane, CH_3Cl, **Methyl chloride,** is obtained from methane or methyl alcohol. At ordinary temperatures it is a gas, that may be condensed to a liquid (by a freezing mixture of ice and calcium chloride). It boils at —22°. Alcohol will dissolve 35 volumes of it, and water 4 volumes.

It is prepared by heating a mixture of 1 part methyl alcohol (wood spirit), 2 parts sodium chloride, and 3 parts sulphuric acid. A better plan is to conduct HCl into boiling methyl alcohol in the presence of zinc chloride (½ part). The disengaged gas is washed with KOH, and dried by means of sulphuric acid. Commercial methyl chloride usually occurs in a compressed condition. It finds application in the manufacture of the aniline dyes, and in producing cold. It is obtained by heating trimethylamine hydrochloride, $N(CH_3)_3.HCl$.

Monochlorethane, C_2H_5Cl, **Ethyl chloride,** is an ethereal liquid, boiling at 12.5°; specific gravity at 0° = 0.921. It is miscible with alcohol, but is sparingly soluble in water.

Preparation.—Heat a mixture of 1 part ethyl alcohol, 2 parts H_2SO_4, and 2 parts NaCl. The gas is washed by passing through warm water and condensed in a strongly cooled receiver. Or HCl may be passed into 95 per cent. alcohol containing ½ part $ZnCl_2$. Heat should be applied.

If heated with water to 100° (in a sealed tube), it changes to ethyl alcohol. The conversion is more rapid with potassium hydroxide. In dispersed sunlight, chlorine acts upon it to form ethylidene chloride, $CH_3.CHCl_2$, and substitution products. Of these C_2HCl_5 was formerly employed as *Æther anæstheticus*.

Monochlorpropane, C_3H_7Cl. Two isomerides are possible:—

Normal propyl chloride, $CH_3.CH_2.CH_2.Cl$, derived from normal propyl alcohol, boils at 46.5°. Its specific gravity is 0.8898 at 0°.

Isopropyl chloride, $CH_3.CHCl.CH_3$, obtained from the corresponding alcohol, and by the union of propylene with HCl, boils at 37°; its specific gravity is 0.874 at 10°.

Monochlor-Butanes, C_4H_9Cl, Butyl chlorides. Four isomerides are possible: two of these arise from the normal and two from the tertiary butane (see p. 43). These (and also their homologues) will be mentioned under the corresponding alcohols.

The *alkyl fluorides* are produced when the potassium salts of the alkyl sulphates are heated with acid fluoride of potassium. The first four members, from *Methyl Fluoride*, CH_3Fl, to *Butyl Fluoride*, C_4H_9Fl, are gases with an ethereal odor.

For the preparation of the bromides from the alcohols, the already made PBr_5 (or PCl_3Br_2) (see p. 92) is not essential. Amorphous phosphorus is taken, alcohol poured over it, and while carefully cooling, bromine is gradually added. The mixture is subsequently distilled:—

$$3C_2H_5.OH + P + 3Br = 3C_2H_5Br + PO_3H_3.$$

The distillate is washed with H_2O and dilute KOH, dried over $CaCl_2$, and then fractionated. The bromides boil from 22–24° higher than their corresponding chlorides.

The bromides may be obtained from the chlorides, by heating with aluminium bromide (*Berichte*, 14, 1709):—

$$3C_2H_5Cl + AlBr_3 = 3C_2H_5Br + AlCl_3.$$

Conversely, the bromides are changed to chlorides through the agency of $HgCl_2$.

Methyl Bromide, CH_3Br—Monobrommethane—boils at + 4.5°; its specific gravity is 1.73 at 0°.

Ethyl Bromide, C_2H_5Br, boils at 39°; its specific gravity is 1.47 at 13°. *Ethylidene Bromide*, CH_3CHBr_2, and *ethylene bromide*, $CH_2Br.CH_2Br$, are obtained from it by the action of bromine.

Propyl Bromide, C_3H_7Br, from the normal alcohol, boils at 71°; its specific gravity is 1.3520 at 20°.

Isopropyl Bromide, C_3H_7Br, from its corresponding alcohol, boils at 60–63°; its specific gravity is 1.3097 at 20°. It is most conveniently obtained by the action of bromine upon isopropyl iodide (*Berichte*, 15, 1904).

Upon boiling with aluminium bromide, or by heating to 250°, normal propyl bromide passes over into the isopropyl bromide (not completely, however, *Berichte*, 16, 391). Such a transposition, due to displacement of the atoms in the molecule, occurs rather frequently, and is termed *molecular transposition*. In many instances it may be explained by the formation of intermediate products. Thus, it may be assumed that the normal propyl bromide, $CH_3.CH_2.CH_2.Br$, at first breaks up into propylene, $CH_3.CH:CH_2$ and HBr (see p. 93), which then, according to a common rule of addition (p. 92), unite with the propylene to isopropyl bromide, $CH_3.CHBr.CH_3$. Similarly, isobutyl bromide, $(CH_3)_2.CH.CH_2.Br$, changes at 240° to tertiary butyl bromide, $(CH_3)_2.CBr.CH_3$. The transpositions occurring on heating the halogen hydrides with the alcohols may be explained in the same manner.

The iodides are obtained just like the bromides, that is, by heating a mixture of the alcohols, phosphorus (yellow or amorphous) and iodine. Concentrated HI converts the alcohols into iodides:—

$$C_2H_5.OH + HI = C_2H_5I + H_2O.$$

Excess of HI, however, again reduces them. (Compare p. 91.)

The polyhydric alcohols (containing several hydroxyl groups) also yield mono-iodides:—

$$\begin{aligned} C_2H_4(OH)_2 &+ 3HI = C_2H_5I + I_2 + 2H_2O \\ C_3H_5(OH)_3 &+ 5HI = C_3H_7I + 2I_2 + 3H_2O \\ C_4H_6(OH)_4 &+ 7HI = C_4H_9I + 3I_2 + 4H_2O \\ C_6H_8(OH)_6 &+ 11HI = C_6H_{13}I + 5I_2 + 6H_2O. \end{aligned}$$

The mechanism of the reaction will be more carefully studied when we reach allyl and isopropyl iodides.

Many iodides can be obtained from the chlorides by heating with AlI_3 (or CaI_2) *Berichte*, **16**, 392, and **19**, Ref. 166):

$$3C_3H_7Cl + AlI_3 = 3C_3H_7I + AlCl_3.$$

In some cases HI accomplishes the same result. Conversely the iodides can be changed to chlorides by heating with mercuric, cupric or stannic chlorides:—

$$2C_3H_7I + HgCl_2 = 2C_3H_7Cl + HgI_2.$$

Free chlorine and bromine can also replace iodine directly:—

$$C_2H_5I + Cl_2 = C_2H_5Cl + ICl.$$

As to the action of various metallic haloids upon organic chlor-, brom-, and iodo- derivatives, see *Ann.*, 225, 146, 171, and 231, 257. These transpositions are, in general, determined by the thermo-chemical deportment of the compounds.

On exposure to the air the iodides soon become discolored by deposition of iodine. The iodides of the secondary and tertiary alcohols are easily converted by heat into alkylens, C_nH_{2n} and HI. Their boiling points are about 33° higher than those of the corresponding bromides.

Methyl Iodide, CH_3I, is a heavy, sweet-smelling liquid, boiling at 45°, and has a sp. gr. = 2.19 at 0°. In the cold it unites with H_2O to form a crystalline hydrate, $2CH_3I + H_2O$.

Ethyl Iodide, C_2H_5I, is a colorless, strongly refracting liquid, boiling at 72° and having a sp. gr. of 1.975 at 0°.

Preparation.—Pour 5 parts alcohol (90 per cent.) over 1 part amorphous phosphorus, then gradually add 10 parts iodine and distil. The distillate is poured back on the residue and redistilled. It is advisable to previously dissolve the iodine in alcohol or ethyl iodide, and add this to the alcohol containing phosphorus. In this case yellow phosphorus may be employed.

Propyl Iodide, C_3H_7I, boils at 102°, and has a specific gravity of 1.7427 at 20°.

Isopropyl Iodide, C_3H_7I, is formed from isopropyl alcohol, propylene glycol, $C_3H_6(OH)_2$, or from propylene, and is most conveniently prepared by distilling a mixture of glycerol, amorphous phosphorus and iodine:—

$$C_3H_5\,(OH)_3 + 5HI = C_3H_7I + 2I_2 + 3H_2O.$$

Here we have allyl iodide produced first (see p. 98), and this is further changed to propylene and isopropyl iodide:—

$$\underset{\text{Allyl Iodide.}}{CH_2 = CH - CH_2I} + HI = \underset{\text{Propylene.}}{CH_2 = CH - CH_3} + I_2,$$

and

$$\underset{\text{Propylene.}}{CH_2 = CH - CH_3} + HI = \underset{\text{Isopropyl Iodide.}}{CH_3 - CHI - CH_3}.$$

Preparation.—300 gr. iodine and 200 gr. glycerol (diluted with an equal volume of H_2O) are placed in a tubulated retort, and 55 gr. of yellow phosphorus added gradually. The portion passing over first is returned and redistilled. To remove admixed allyl iodide from the isopropyl iodide, conduct it into HI and let stand. (*Annalen*, 138, 364.)

Isopropyl iodide boils at 89.9°, and has a specific gravity of 1.7033 at 20°.

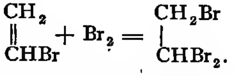
The higher alkyl iodides are mentioned under the corresponding alcohols.

HALOGEN DERIVATIVES—$C_nH_{2n-1}X$ and $C_nH_{2n-2}X_2$.

As a general thing, the halogen substitution products of the unsaturated hydrocarbons cannot be prepared by direct action of the halogens, since addition products are apt to result (p. 91). They are produced, however, by the moderated action of alcoholic potash, or Ag_2O, upon the substituted hydrocarbons $C_nH_{2n}X_2$. This reaction occurs very readily if we employ the addition products of the olefines:—

$$\underset{\substack{\text{Ethylene}\\\text{Chloride.}}}{C_2H_4Cl_2} + KOH = \underset{\substack{\text{Monochlor-}\\\text{ethylene.}}}{C_2H_3Cl} + KCl + H_2O.$$

When the alcoholic potash acts very energetically the hydrocarbons of the acetylene series are formed (p. 86). Being unsaturated compounds they unite directly with the halogens, and also the hydrides of the latter:—



$$\begin{array}{l}CH_2\\ \|\\ CHBr\end{array} + Br_2 = \begin{array}{l}CH_2Br\\ |\\ CHBr_2.\end{array}$$

Monochlorethylene, $C_2H_3Cl = CH_2{:}CHCl$, or Vinyl chloride (the group $CH_2{:}CH$ is called Vinyl), derived from ethylene chloride, $CH_2Cl.CH_2Cl$, and (although with greater difficulty) from ethylidene chloride, $CH_3.CHCl_2$, is a gas with garlic-like smell, liquefying at —18° and polymerizing in the sunlight.

Monobromethylene, C_2H_3Br, Vinyl bromide, is obtained by boiling ethylene bromide with aqueous potassium hydroxide. It possesses an odor similar to that of the chloride, boils at 16°, and has a specific gravity of 1.52. Under certain conditions, in sunlight, for example, it is converted into a solid polymeric modification. It dissolves readily in concentrated sulphuric acid, and if the solution be boiled with water crotonaldehyde results (from acetaldehyde that is formed previously). Vinyl bromide does not react with CNAg or CNK, and, indeed, does not appear capable of double decompositions. (*Berichte*, 14, 1532.)

Ethylene Mono-iodide, C_2H_3I, Vinyl iodide, is obtained from ethylene and ethylidene iodides, by the aid of alcoholic potash, and boils at 55°; its specific gravity is 1.98.

Ethylene Dichlorides and Dibromides:—

$CH_2 = CCl_2$ — Ethylene α-dichloride. $CHCl = CHCl$ — Ethylene β-dibromide.

Ethylene α-Dichloride (unsymmetrical) is formed from ethylene chloride, $CH_2Cl.CHCl_2$, by the action of alcoholic potash, and boils at 37°. **Ethylene β-dichloride** (symmetrical) is formed by the union of acetylene, C_2H_2, with $SbCl_5$. It boils at 55°. **Ethylene α-Dibromide**, from bromethylene bromide, $CH_2Br.CHBr_2$, boils at 91°. **Ethylene β-dibromide**, formed from acetylene by addition of Br_2, and from acetylene tetrabromide, $C_2H_2Br_4$, through the agency of zinc, boils at 110°. Ethylene α-dibromide, with benzene and $AlCl_3$, yields ethylene diphenyl, $CH_2{:}C(C_6H_5)_2$; but from ethylene β-dibromide dibenzyl is obtained $C_6H_5.CH_2.CH_2\,C_6H_6$. (*Berichte*, 16, 622.)

The unsymmetrical products are inclined to polymerize. This is not the case with the symmetrical (*Berichte*, 12, 2076). The ethylene mono-haloids polymerize similarly, but ethylene itself does not change. It appears, too, that the power of direct union with oxygen, thereby yielding the chloranhydrides of substituted acetic acids, is only possessed by the unsymmetrical substitution products, $CH_2{:}CBr_2 + O = CH_2.Br.COBr$. (*Berichte*, 16, 2918.) For the course of the reaction see *Ber.*, 21, 3356.

Two isomeric *Di-iodo-ethylenes*, $CH_2I.CH_2I$, are said to form when acetylene unites with iodine in an alcoholic solution (*Ann.*, 178, 118).

Three different mono-halogen products are derived from propylene, $CH_3 - CH = CH_2$:—

(1) $CH_3 - CH = CHX$ (2) $CH_3 - CX = CH_2$ (3) $CH_2X - CH = CH_2$.
α-Derivatives. β-Derivatives. γ-Derivatives.

(1) The α-derivatives are obtained from the propylidene compounds, $CH_3 \cdot CH_2.CHX_2$ (from propyl aldehyde), when the latter are heated with alcoholic potassium hydroxide, while from the addition products of propylene, $CH_3.CHBr.CH_2.Br$, we obtain the β-derivatives at the same time. Propylene α-chloride boils at 35° (see *Ber.*, 20, 1040 for a geometrical, isomeric α-chlorpropylene). α-Brompropylene boils at 59–60°; its specific gravity at 19° is 1.428.

(2) The β-derivatives, $CH_3.CX:CH_2$, are prepared in pure condition from the halogen compounds derived from acetone. Propylene β-chloride boils at 23°; its sp. gr. at 9° is 0.918. Propylene β-bromide boils at 48°; its sp. gr. at 19° is 1.364.

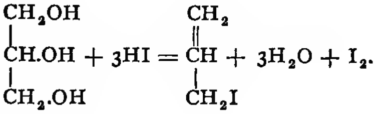
Continued heating with alcoholic potash causes both α- and β-varieties to pass into allylene. Propylene β-bromide combines in the cold with HBr to form acetal bromide, $CH_3.CBr_2.CH_3$, while the alpha variety only unites with it at 100°, and then yields a mixture of propylene and propylidene bromide (p. 101). Sulphuric acid and water, aided by heat, convert the β-chloride into acetone, $CH_3.CO.CH_3$. The α-products especially appear to react with far more difficulty (like ethylene monochloride) than the β-varieties (compare the chlorides of styrolene).

(3) The γ-derivatives of propylene, $CH_2X - CH = CH_2$, are designated *Allyl haloids*, because they correspond to allyl alcohol, $CH_2:CH.CH_2OH$. The allyl group $(CH_2:CH.CH_2)$ occurs in some vegetable substances (mustard oil, oil of garlic). Heated with alcoholic potash the allyl haloids yield allyl ethyl ether, $C_3H_5.O.C_2H_5$. The ease with which they undergo transpositions is characteristic, and serves to distinguish them from the α- and β-products.

Allyl chloride, C_3H_5Cl, is formed by the action of PCl_3 or HCl upon allyl alcohol, or by the transposition taking place between allyl iodide and $HgCl_2$ (p. 95). It is a liquid with an odor resembling that of leeks; boils at 46°, and has a specific gravity of 0.9379 at 20°. If heated to 100° with concentrated hydrochloric acid it yields propylene chloride, $CH_3.CHCl.CH_2Cl$ (trimethylene chloride, $CH_2Cl.CH_2.CH_2Cl$, is not produced).

Allyl Bromide, C_3H_5Br, boils at 70-71°; its specific gravity at 0° equals 1.461. Upon warming to 100° C., it combines with concentrated HBr to form trimethylene bromide, $CH_2Br.CH_2.CH_2Br$ (see p. 102).

Allyl Iodide, C_3H_5I, is obtained from allyl alcohol, or better, from glycerol, by the action of HI, or iodine and phosphorus (compare p. 95):—



$$\begin{array}{l} CH_2OH \\ | \\ CH.OH \\ | \\ CH_2.OH \end{array} + 3HI = \begin{array}{l} CH_2 \\ \| \\ CH \\ | \\ CH_2I \end{array} + 3H_2O + I_2.$$

We may suppose that at first $CH_2I.CHI.CH_2I$ forms, but is subsequently decomposed into $CH_2:CH.CH_2I$ and I_2. With excess of HI or phosphorus iodide, allyl iodide is further converted into propylene and isopropyl iodide (p. 96).

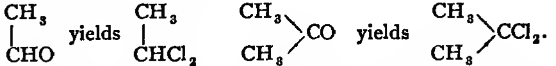
Preparation.—150 parts of concentrated glycerol and 100 parts pulverized iodine are introduced into a tubulated retort, and 60 parts of yellow phosphorus gradually added to the mixture. When the first action has passed away, the allyl iodide is distilled off, and the distillate washed with dilute potassium hydroxide. When larger quantities are employed explosions sometimes occur; these may be obviated if the operation be carried out in a stream of CO_2 gas. (Compare *Annalen*, 185, 191 and 226, 206.)

Allyl iodide is a colorless liquid, with a leek-like odor, boiling at 101°. Its specific gravity equals 1.789 at 16°. By continued shaking of allyl iodide (in alcoholic solution) with mercury, C_3H_5HgI separates in colorless leaflets (see mercury ethyl). Iodine liberates pure allyl iodide from this:—

$$C_3H_5HgI + I_2 = C_3H_5I + HgI_2.$$

DIHALOGEN COMPOUNDS $C_nH_{2n}X_2$.

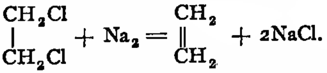
These derivatives of the paraffins arise by direct substitution, by the addition of halogens to the alkylens, $C_n H_{2n}$, and the halogen hydrides to the substituted alkylens, $C_n H_{2n-1} X$; and by the action of the phosphorus haloids upon the aldehydes and ketones (p. 92). The products thus obtained are of like composition, and are partly identical, partly isomeric. The direct addition products, $C_n H_{2n}X_2$, have the halogen atoms attached to two adjacent carbon atoms (see p. 86). In the compounds resulting from the replacement of the oxygen of aldehydes and ketones, both halogen atoms are in union with the same carbon atom:—



$$\begin{array}{c} CH_3 \\ | \\ CHO \end{array} \text{ yields } \begin{array}{c} CH_3 \\ | \\ CHCl_2 \end{array} \qquad \begin{array}{c} CH_3 \\ CH_3 \end{array}\!\!>\!CO \text{ yields } \begin{array}{c} CH_3 \\ CH_3 \end{array}\!\!>\!CCl_2.$$

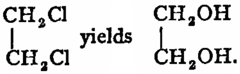
Aldehyde. Acetone.

Heated with alcoholic potash, the addition products pass into the compounds $C_n H_{2n-1} X$ and $C_n H_{2n-2}$ (page 96). The alkylens result when the dihalogen compounds are heated with sodium:—



$$\begin{array}{c} CH_2Cl \\ | \\ CH_2Cl \end{array} + Na_2 = \begin{array}{c} CH_2 \\ \| \\ CH_2 \end{array} + 2NaCl.$$

Those derivatives, in which the halogens are attached to different carbon atoms, are capable of forming glycols:—



$$\begin{array}{c} CH_2Cl \\ | \\ CH_2Cl \end{array} \text{ yields } \begin{array}{c} CH_2OH \\ | \\ CH_2OH. \end{array}$$

Methylene Chloride, Dichlormethane, CH_2Cl_2, is produced in the chlorination of CH_3Cl, by the action of Cl upon CH_2I_2 or CH_3I, and by the reduction of chloroform by means of zinc and ammonia. It is a colorless liquid, boiling at 41°, and having a specific gravity of 1.36 at 0°.

Methylene Bromide, CH_2Br_2, results on heating CH_3Br with bromine (together with $CHBr_3$), and by the action of bromine upon methylene iodide. It boils at 81° (98.5°) and has a specific gravity of 2.493 at 0°.

Methylene Iodide, CH_2I_2, is produced in the action of sodium alcoholate upon iodoform, CHI_3, and is best prepared by heating $CHCl_3$ or CHI_3 with fuming HI to 130°:—

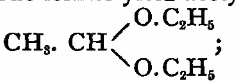
$$CHCl_3 + 4HI = CH_2I_2 + I_2 + 3HCl.$$

It is a colorless liquid with a specific gravity of 3.34. It boils, with decomposition, about 182°. At low temperatures it forms shining leaflets, melting at + 4°.

The empirical formula $C_2H_4X_2$ has two possible structures:—

$$\begin{array}{ccc} CH_2X & & CH_3 \\ | & \text{and} & | \\ CH_2X & & CHX_2 \end{array}$$

Ethylene Compounds. Ethylidene Compounds.

The first originate from ethylene, the second from aldehyde $CH_3.COH$. The former yield acetylene with alcoholic potash, the latter acetal,  $CH_3.CH\begin{cases}O.C_2H_5\\O.C_2H_5\end{cases}$; the former yield glycol, the latter do not.

Ethylene Chloride, $C_2H_4Cl_2$, is obtained by the direct union of equal volumes of ethylene and chlorine gas, or by conducting ethylene through warm $SbCl_5$. It is a colorless, pleasant-smelling liquid, of specific gravity 1.2521 at 20°, and boils at 84°.

Ethylidene Chloride, $CH_3.CHCl_2$, is produced by the chlorination of ethyl chloride (both gases are conducted over animal charcoal heated to about 300°) and from aldehyde (better paraldehyde) by the action of PCl_5, or phosgene (*Ber.*, **18**, 578). On a large scale it appears as a by-product in the preparation of chloral. It is a liquid, smelling like chloroform, with a specific gravity of 1.1743 at 20°, boils at 57.7°, and is employed as an anæsthetic. By further chlorination it yields $CH_3.CCl_3$ together with a little $CH_2Cl.CHCl_2$. When $AlCl_3$ is present, the latter is the only product.

Ethylene Bromide, $C_2H_4Br_2$, is formed by saturating bromine with ethylene gas (*Annalen*, **192**, 244), and is an oily, pleasant-smelling liquid, boiling at 131°; its specific gravity is 2.178 at 20°. At 0° it solidifies to a crystalline mass, fusing at + 9°.

Ethylidene Bromide, $C_2H_4Br_2 = CH_3.CHBr_2$, formed together with ethylene bromide by the bromination of $C_2H_5.Br$ (in presence of $AlBr_3$, only ethylene bromide is produced), is obtained by the action of PCl_3Br_2 upon aldehyde. It boils at 110.5°, and has a specific gravity of 2.082 at 21°.

The formation of ethylene and ethylidene bromides from monobromethylene is quite interesting. When the latter is heated with very concentrated HBr, ethylene bromide forms, while with more dilute acid ethylidene bromide results.

Ethylene Iodide, $C_2H_4I_2$, is produced in the union of iodine with ethylene, by conducting the latter into a solution of iodine in alcohol. It crystallizes from alcohol in brilliant needles, which rapidly become yellow on exposure to light. The compound melts at 81°, and at higher temperatures decomposes into C_2H_4 and I_2. It may be distilled in an atmosphere of ethylene gas without decomposition.

Ethylidene Iodide, $CH_3.CHI_2$, is obtained from ethylidene chloride by the action of aluminium iodide (p. 95). It boils at 178°, sustaining partial decomposition; its specific gravity is 2.84 at 0°. It is also formed by the addition of 2HI to acetylene.

Four different di-halogen products are derived from propane C_3H_8:—

(1) $CH_3.CH_2.CHX_2$. (2) $CH_3.CX_2.CH_3$. (3) $CH_3.CHX.CH_2X$, and (4) $CH_2X.CH_2.CH_2X$.

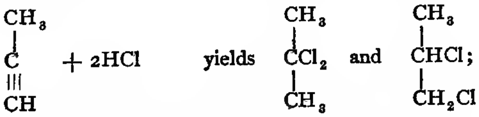
(1) Derivatives of the first structure, called propylidene compounds, arise from propyl aldehyde, $CH_3.CH_2.CHO$, by the action of PCl_5.

Propylidene Chloride, $C_3H_6Cl_2$, is a liquid, with an odor resembling that of leeks, and boiling at 84–87°. Its specific gravity at 10° is 1.443. The bromide, $C_3H_6Br_2$, from propylene *α*-bromide, boils at 130°.

(2) Derivatives of the formula $CH_3.CX_2.CH_3$ are obtained from acetone by the action of PCl_5 and PBr_5:—

$$\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right>CO \quad \text{yields} \quad \left.\begin{matrix}CH_3\\CH_3\end{matrix}\right>CX_2.$$

Dimethyl Methylene Chloride, $C_3H_6Cl_2 = CH_3.CCl_2.CH_3$, methyl chloracetol or acetone chloride, is formed by the addition of 2HCl to allylene (together with propylene chloride):—



$$\begin{matrix}CH_3\\|\\C\\|||\\CH\end{matrix} + 2HCl \quad \text{yields} \quad \begin{matrix}CH_3\\|\\CCl_2\\|\\CH_3\end{matrix} \text{ and } \begin{matrix}CH_3\\|\\CHCl;\\|\\CH_2Cl\end{matrix}$$

and by the chlorination of isopropyl chloride, $CH_3.CHCl.CH_3$.

It is a colorless liquid, boiling at 69–70°, and having a specific gravity 1.827 at 16°. *β*-Monochlorpropylene is obtained from it by the action of alcoholic potash (p. 98). Heated to 150° with water, it changes in part to acetone.

Dimethyl Methylene Bromide, $C_3H_6Br_2$, from acetone, and from allylene, by the addition of 2 HBr, boils at 113–116°; its specific gravity at 0° is 1.875.

(3) We get the derivatives of the structure $CH_3.CHX.CH_2X$ by uniting propylene with the halogens:—

$$CH_3 - CH = CH_2 \text{ affords } CH_3.CHX.CH_2X.$$

This class passes into propylene glycol when acted upon by moist silver oxide; with alcoholic potash they yield $CH_3.CX:CH_2$, and allylene.

Propylene Chloride, $C_3H_6Cl_2 = CH_3.CHCl.CH_2Cl$, is produced, together with acetone chloride, when chlorine acts in sunlight upon isopropyl-chloride (in presence of iodine the chlorination extends only to propylene chloride). It boils at 97°, and has a specific gravity of 1.165 at 14°.

Propylene Bromide, $C_3H_6Br_2 = CH_3.CHBr.CH_2Br$, is a liquid boiling at 141°. It is formed in the bromination of propyl bromide and isopropyl bromide. Its specific gravity at 17° equals 1.946. Propionic aldehyde and acetone result when propylene bromide or the chloride is heated, together with H_2O, to 200°.

Propylene Iodide, $C_3H_6I_2 = CH_3.CHI.CH_2I$, results by the union of iodine with propylene at 50°. It is a colorless oil, that cannot be distilled without suffering decomposition.

(4) The products of the formula $CH_2X.CH_2.CH_2Cl$ are designated trimethylene derivatives.

Trimethylene Chloride, $C_3H_6Cl_2 = CH_2Cl.CH_2.CH_2Cl$, is obtained by heating the corresponding bromide with mercuric chloride to 160°. It is an agreeably smelling liquid, that boils at 119°, and at 15° has a sp. gr. = 1.201.

Trimethylene Bromide, $C_3H_6Cl_2$, results on heating allyl bromide, $CH_2:CH.CH_2Br$, with concentrated hydrobromic acid. Propylene bromide is produced at the same time. This can be removed by fractional distillation. (With HCl the only product of allyl chloride is propylene chloride, $CH_3.CHCl.CH_2Cl$.) It is obtained in a purer form on saturating allyl bromide with HBr in the cold, and letting the whole stand some time (*Annalen*, 197, 184). Trimethylene bromide is a colorless liquid, boiling at 164°, and has a specific gravity of 2.01 at 0°. When treated with alcoholic potash, it yields allyl bromide and allyl ethyl ether. Trimethylene is the product with sodium (p. 83). Continued boiling with water converts it into trimethylene glycol.

Trimethylene Iodide, $C_3H_6I_2$, obtained on heating trimethylene bromide with sodium iodide, is a colorless oil, boiling near 224°.

THE HALOGEN COMPOUNDS $C_nH_{2n-1}X_3$.

Chloroform, $CHCl_3$, Trichlormethane, is formed: by the chlorination of CH_4 or CH_3Cl; by the action of chloride of lime ? upon different carbon compounds, *e. g.*, methyl or ethyl alcohol, acetone, acetic acid; and by heating chloral with aqueous potassium or sodium hydroxide:—

$$\underset{\text{Chloral.}}{CCl_3.CHO} + KOH = CCl_3H + \underset{\text{Potassium Formate.}}{CHKO_2}.$$

In preparing chloroform a mixture of alcohol, bleaching lime, and water is distilled from a capacious retort (*Annalen*, 165, 349). It would be an advantage to substitute acetone for the alcohol. The chloroform produced is carried over with the steam and collects in the bottom of the receiver as a heavy oil. It is purified by shaking with H_2SO_4 and repeated distillation. At present it is generally obtained from chloral. Pure chloroform should not color on the addition of concentrated sulphuric acid.

Chloroform is a colorless liquid of an agreeable ethereal odor and sweetish taste. It solidifies in the cold and melts at — 71°. It boils at 61°, and its specific gravity at 0° equals 1.526. Inhalation of its vapors causes unconsciousness, and at the same time has an anæsthetic effect. It is uninflammable. Chlorine changes it to CCl_4. Potassium formate is produced when chloroform is heated with alcoholic potash:—

$$CHCl_3 + 4KOH = CHO.OK + 3KCl + 2H_2O.$$

The so-called tribasic formic acid ester, $CH(O.C_2H_5)_3$, is produced by treating chloroform with sodium alcoholate. When heated to 180° with aqueous or alcoholic ammonia, it forms ammonium cyanate and chloride. When KOH is present, an energetic reaction takes place at ordinary temperatures. The equation is—

$$CHCl_3 + NH_3 + 4KOH = CNK + 3KCl + 4H_2O.$$

Bromoform, $CHBr_3$, is produced in the same way as chloroform, by the action of bromine and KOH upon methyl and ethyl alcohol. It is a colorless, agreeable-smelling liquid, solidifying at — 9°. It boils at 151° and has a specific gravity 2.83 at 0°.

Iodoform, CHI_3. This compound results when iodine and potash act upon ethyl alcohol, or acetone, aldehyde and other substances containing the methyl group. Pure methyl alcohol, however, does not yield iodoform. (*Berichte*, 13, 1002).

Preparation.—Dissolve 2 parts crystallized soda in 10 parts of water, add 1 part alcohol, bring the whole to 60–80°, and gradually introduce 1 part of iodine. The iodoform that separates is filtered off. By renewed warming of the filtrate with KOH and alcohol, followed by the introduction of chlorine, an additional quantity of iodoform may be obtained.

Iodoform crystallizes in brilliant, yellow leaflets, soluble in alcohol and ether. Its odor is saffron-like. It evaporates at medium temperatures; fuses at 119° and distils over with the aqueous vapor. Digested with alcoholic KOH, or HI, it passes into methylene iodide, CH_2I_2.

Two isomeric tri-halogen derivatives may be obtained from ethane C_2H_6:—

$$CH_3 — CX_3 \text{ and } CH_2X — CHX_2.$$

a-**Trichlor-Ethane,** $CH_3.CCl_3$, is produced (together with $CH_2Cl.CHCl_2$) by the chlorination of ethyl and ethylidene chloride in sunlight. It is a liquid with chloroform-like odor, and boils at 74.1°. Its specific gravity at 0° is 1.346. If heated with KOH it yields potassium acetate:—

$$CH_3.CCl_3 + 4KOH = CH_3.CO.OK + 3KCl + 2H_2O.$$

Treated with sodium alcoholate it yields the tri-ethyl ester $CH_3.C(O.C_2H_5)_3$. Further chlorination of trichlor-ethane produces $CH_2Cl.CCl_3$, boiling at 131°, $CHCl_2.CCl_3$, at 162°, and perchlor-ethane, $CCl_3.CCl_3$ (see p. 105). $CHCl_2.CHCl_2$, from dichlor-aldehyde, boils at 113.7° (*Berichte*, 15, 2563).

β-**Trichlor-Ethane**, $CH_2Cl.CHCl_2$, monochlor-ethylene chloride, is produced by the union of vinyl chloride, $CH_2.CHCl$, with Cl_2, and boils at 113.7°. Its specific gravity at 0° equals 1.422.

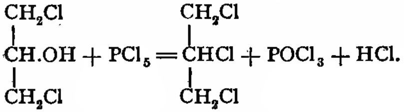
α-**Tribrom-Ethane**, CH_2CBr_3, has not been formed.

β-**Tribrom-Ethane**, CH_2CHBr_2, monobrom-ethylene bromide, forms upon brominating ethyl and ethylene bromides, also by addition of bromine to brom-ethylene, $CH_2.CHBr$. It boils at 187°; its specific gravity at 21° equals 2.610.

Trisubstituted propane, $C_3H_5X_3$, can have five structural forms. The most important derivatives are those having the formula $CH_2X.CHX.CH_2X$. They correspond to glycerol, $CH_2(OH).CH(OH).CH_2(OH)$. The trivalent group $CH_2.CH.CH_2$, present in them, is termed *glyceryl.* They are produced by the addition of chlorine or bromine to allyl chloride and bromide:—

$$CH_2{:}CH.CH_2.Cl + Cl_2 = CH_2Cl.CHCl.CH_2Cl;$$

or by the action of PCl_5 upon dichlorhydrin, which is derived from glycerol:—



$$\begin{array}{l}CH_2Cl\\ |\\ CH.OH\\ |\\ CH_2Cl\end{array} + PCl_5 = \begin{array}{l}CH_2Cl\\ |\\ CHCl\\ |\\ CH_2Cl\end{array} + POCl_3 + HCl.$$

Moist silver oxide converts them into glycerol.

Glyceryl Chloride, $C_3H_5Cl_3$, allyl trichloride, trichlorhydrin, is a liquid with an odor resembling that of chloroform, and boiling at 158°. Its specific gravity at 15° equals 1.417.

Glyceryl Bromide, $C_3H_5Br_3$, tribromhydrin, is best obtained by the action of bromine upon allyl iodide:—

$$C_3H_5I + 4Br = C_3H_5Br_3 + IBr.$$

It crystallizes in colorless, shining leaflets, fusing at 16°, and boiling at 220°.

Glyceryl Iodide, $C_3H_5I_3$, appears not to exist. It decomposes at once into allyl iodide and I_2 (p. 98).

Among the higher substitution products may be mentioned the following carbon haloids:—

Tetrachlor-methane or Carbon Tetrachloride, CCl_4, is formed by the action of chlorine upon chloroform, and by conducting a mixture of Cl and CS_2 through tubes heated to redness.

Preparation. Chlorine is conducted through boiling chloroform exposed to sunlight, or through a mixture of CS_2 and $SbCl_5$. In the latter case, sulphur chloride is formed at the same time. This may be decomposed by shaking with KOH.

It is a pleasant-smelling liquid, boiling at 76–77°. Its specific gravity is 1.631 at 0°. At — 30° it solidifies to a crystalline mass. Heated with alcoholic KOH, it decomposes according to the following equation:—

$$CCl_4 + 4KOH = CO_2 + 2H_2O + 4KCl.$$

When the vapors are conducted through a red-hot tube, decomposition occurs; C_2Cl_4 and C_2Cl_6 are produced.

Tetrabrommethane, CBr_4, obtained by the action of brom-iodide upon bromoform or CS_2, crystallizes in shining plates, melting at 92.5°, and boiling, with but little decomposition, at 189°.

Tetraiodomethane, CI_4, carbon iodide, is formed when CCl_4 is heated with aluminium iodide (p. 95). It crystallizes from ether in dark red, regular octahedra, of specific gravity 4.32 at 20°. On exposure to air it decomposes into CO_2 and I. Heat accelerates the decomposition.

Perchlorethane, C_2Cl_6, is the final product in the action of Cl upon C_2H_5Cl or $C_2H_4Cl_2$. It is a crystalline mass, with a camphor-like odor and specific gravity 2.01. It melts (in a capillary tube) at 187–188°. At ordinary pressure it vaporizes without fusing, as its critical pressure (compare Inorganic Chemistry), lies above 760 mm. It boils at 185°.5 under a pressure of 776.7 mm. It is readily soluble in alcohol and ether. When its vapors are conducted through tubes heated to redness, it breaks up into Cl_2 and **ethylene perchloride**, C_2Cl_4. This is a mobile liquid, boiling at 121°. Its specific gravity at 20° is 1.6226.

Perbromethane, C_2Br_6, is a colorless crystalline compound, sparingly soluble in alcohol and ether. At 200° it decomposes into Br_2 and ethylene perbromide, C_2Br_4, which consists of colorless crystals, melting at 53°.

Perchlormesole, C_4Cl_6, is formed on heating hexyl iodide or amyl chloride with ICl_3. It melts at 39°, and boils at 284° (*Berichte*, 10, 804).

NITRO-DERIVATIVES OF THE HYDROCARBONS.

By this designation is understood compounds of carbon in which the hydrogen combined with the latter is replaced by the monovalent nitro-group, NO_2. The carbon is directly united to the nitrogen by one affinity. A universal method for the production of nitro-compounds consists in acting upon the hydrocarbon derivatives with concentrated nitric acid:—

$$C_6H_6 + NO_3H = C_6H_5 (NO_2) + H_2O.$$

The reaction is promoted by the presence of H_2SO_4, which serves to combine with the water that is generated. The fatty bodies capable of this reaction are exceptional; the benzene derivatives, however, readily yield nitro-derivatives.

A common method for the preparation of the mono-nitro derivatives of fatty hydrocarbons—the **nitro-paraffins**—consists in heating the iodides of the alcohol radicals with silver nitrite (*V. Meyer*):—

$$C_2H_5I + AgNO_2 = C_2H_5.NO_2 + AgI.$$

The isomeric esters of nitrous acid, such as $C_2H_5.O.NO$ arise (see *Berichte*, 15, 1574) in this reaction. From this we would infer that silver nitrite conducted itself as if apparently consisting of $AgNO_2$ and Ag.O.NO. (Potassium nitrite does not act like $AgNO_2$). Since, however, CH_3I only yields nitromethane, and the higher alkyliodides decompose more readily into alkylens the greater the quantity of nitrous acid esters, it would appear that the formation of esters is influenced by the production of alkylens, which afterwards form esters by the union with HNO_2 (compare *Annalen*, 180, 157, and *Ber.*, 9, 529).

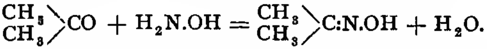
The nitro-compounds generally decompose with an explosion, if quickly heated. They are not broken up by sodium or potassium hydroxide. These reagents convert the isomeric nitrous esters, with ease, into nitrous oxide and alcohol. Nascent hydrogen reduces the mono-nitro derivatives to amido-compounds, by converting the group NO_2 into NH_2—the amido group:—

$$C_2H_5.NO_2 + 3H_2 = C_2H_5.NH_2 + 2H_2O.$$

The compounds resulting from the action of nitrogen tetroxide upon the alkylenes, *e. g.*, $C_2H_4N_2O_4$, are not nitro-derivatives; they belong to the class known as *nitrosates*.

The **nitroso-compounds**, containing the group NO attached to carbon, are classified with the nitro-compounds. Few of them are known. The pseudo-nitrols probably belong to this class (p. 110). Most of the compounds resulting from the action of nitrous acid are isonitroso- and not nitroso-derivatives (*Ber.*, 20, 331; 21, 1294). The **nitroso-amines**, $(CH_3)_2N.NO$, form another class of nitroso-compounds. In them the nitroso-group is linked to nitrogen. Their treatment will be found under the corresponding amines.

The **isonitroso-**, or **oximido-compounds**—$(CH_3)_2.C:N.OH$—containing the bivalent oximid group $= N.OH$ linked to carbon—are isomeric with the above nitroso-derivatives. They are formed, especially when nitrous acid acts upon bodies containing the group CH_2 attached to two CO groups. They also result from the action of hydroxylamine upon ketones R.CO.R, and aldehydes R.COH:—



$$\left.\begin{matrix}CH_5\\CH_3\end{matrix}\right>CO + H_2N.OH = \left.\begin{matrix}CH_3\\CH_3\end{matrix}\right>C:N.OH + H_2O.$$

Consequently these isonitroso-compounds will be treated with the derivatives from which they originate. The so-called alkylnitrolic-acids may be included with them. (See p. 109.)

The nitroso derivatives (of the benzene class and the nitroso-amines) give blue colorations in their action upon a mixture of phenol and sulphuric acid, especially after dilution with water and super-saturation with alkali. The isonitroso-compounds, however, do not yield this reaction (*Berichte*, 15, 1529).

NITRO-PARAFFINS $C_nH_{2n+1}(NO_2.)$

Those formed by the action of silver nitrite upon the alkyl-iodides are colorless liquids almost insoluble in water. They are rather stable, distil without decomposition and decompose with difficulty. It is worthy of note that they possess an acidic character (distinctive from the halogen substitution products): this is indicated by the substitution of metals for one hydrogen atom, through the action of alkaline hydroxides:—

$$CH_3.CH_2(NO_2) + KOH = CH_3.CHK(NO_2) + H_2O.$$

The nitro-group always exerts such an acidic influence upon hydrogen linked to carbon; the further addition of halogens or nitro-groups increases the same, but it is confined to the hydrogen linked to the same carbon atom. Thus the compounds: $CH_3.CHBr(NO_2)$, brom-nitroethane, $CH_3.CH(NO_2)_2$, di-nitroethane, $CH(NO_2)_3$, nitroform, etc., are strong acids, while $CH_3.CBr_2(NO_2)$ and $(CH_3)_2C(NO_2)_2$, β-dinitro-propane, etc., possess neutral reaction and do not combine with bases.

The nitro-paraffins may be viewed as isonitroso-compounds (*Ber.*, 20, 531, and Ref. 296).

For compounds resulting from the action of sodium ethylate and the alkyl iodides upon the nitro ethanes, *e.g.*, C_6H_9NO, see *Ber.*, 21, Ref. 58 and 710.

Zinc ethide converts the nitro-paraffins into tri-ethyl-hydroxylamines (*Ber.*, 22, Ref. 250). Brom-nitro ethane, $CH_3.CHBr(NO_2)$, and zinc methyl yield nitro-isopropane.

Nitromethane, $CH_3.NO_2$, is produced by boiling chloracetate of potassium, $CH_2Cl.COOK$, with potassium nitrite. In this instance it is very probable nitro-acetic acid is first formed, but it subsequently breaks up into nitromethane and carbon dioxide:—

$$CH_2.NO_2.CO_2H = CH_3NO_2 + CO_2.$$

It is an agreeable-smelling, mobile liquid, sinking in water and boiling at 101°. Mixed with an alcoholic sodium hydroxide solution it gives a crystalline precipitate, $CH_2Na(NO_2) + C_2H_6O$, which loses alcohol on standing over sulphuric acid. Salts of the heavy metals precipitate metallic compounds (like $CH_2Ag(NO_2)$) from the aqueous solution. These are in most cases violently explosive. Nitromethane is liberated again from the salts by mineral acids.

Heated with concentrated HCl to 150° nitromethane breaks up into formic acid and hydroxylamine:—

$$CH_3.(NO_2) + H_2O = CH_2O_2 + NH_2.OH.$$

Chlorine water converts sodium nitromethane into nitrochlormethane, $CH_2Cl.(NO_2)$, which is an oil boiling at 122°. In like manner, through the agency of bromine, we obtain bromnitromethane, $CH_2Br(NO)_2$, a pungent smelling oil, boiling at 144°, from which are also prepared dibrom-, and tribrom-nitromethane, $CHBr_2(NO_2)$ and $CBr_3(NO_2)$.—Bromopicrin (p. 113). The first three bodies have an acid reaction and dissolve in alkalies.

Nitroethane, $C_2H_5.NO_2$, is similar to nitromethane. It boils at 113–114° and its specific gravity at 13° equals 1.058. Nascent hydrogen converts it into $C_2H_5.NH_2$. Heated to 140° with concentrated hydrochloric acid, it decomposes into acetic acid and hydroxylamine. Ferric chloride imparts a blood-red color and copper sulphate a dark green to the sodium compound.

Bromine converts nitroethane, in alkaline solution, into bromnitroethane, $CH_3.CHBr(NO_2)$, an oil with a pungent odor, boiling at 147°, and into dibromnitroethane, $CH_3.CBr_2NO_2$, boiling at 105°. The first reacts strongly acid and dissolves in NaOH to $CH_3.CNaBr(NO_2)$; the second is neutral and insoluble in alkalies.

α–**Nitropropane,** $C_3H_7.NO_2 = CH_3.CH_2.CH_2.NO_2$, boils at 125–127°.

β–**Nitropropane,** $(CH_3)_2CH.NO_2$, boils from 115–117°. Both have an acid reaction and yield salts with the alkalies.

Brom-α-nitropropane, $CH_3.CH_2.CHBr(NO_2)$, boiling at 160–165°, has a strong acid reaction and dissolves in alkalies. On the other hand, dibrom-α-nitropropane, $CH_3.CH_2.CBr_2(NO_2)$, boiling at 185°, is a neutral compound insoluble in alkalies. Brom-β-nitropropane, $(CH_3)_2CBr(NO_2)$, boiling at 148–150° is also a neutral compound (see p. 107).

Nitrobutanes, $C_4H_9.NO_2$ (compare Butyl alcohols). Normal nitrobutane, $CH_3.CH_2.CH_2.CH_2.NO_2$, boils at 151° and yields normal butylamine by reduction. *Secondary nitrobutane,* $CH_3.CH_2.CH(NO_2).CH_3 = \begin{matrix} C_2H_5 \\ CH_3 \end{matrix} \!\!>\! CH.NO_2$, boils about 140°. *Nitroisobutane,* $(CH_3)_2CH.CH_2.NO_2$, boils at 137–140°, and has an odor resembling that of peppermint. The three nitrobutanes are acid, dissolve in alkalies and yield bromine derivatives. Tertiary nitrobutane, $(CH_3)_3C.NO_2$, on the contrary, boiling at 120° is a neutral compound, insoluble in alkalies.

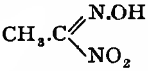
Nitroisoamyl, $C_5H_{11}.NO_2$, obtained from amyl-alcohol of fermentation, boils at 150–160° and yields metallic compounds.

Nitropropylene, $C_3H_5.NO_2$, allyl nitryl, from allyl bromide, is an oil boiling at 96°.

Nitroalkylens, $C_n H_{2n-1}(NO_2)$, are formed in the action of nitric acid upon some alkylens and tertiary alcohols. Thus there is a nitro-butylene, $C_4H_7(NO_2)$, obtained from isobutylene, $(CH_3)_2C{:}CH_2$, and trimethyl-carbinol $(CH_3)_3C.OH$. It boils about 156°. A nitroamylene, $C_5H_9(NO_2)$, is also obtained from dimethyl ethyl carbinol $\left.\begin{matrix} (CH_3)_2 \\ C_2H_5 \end{matrix}\right\} C.OH$. Upon reduction, these nitroalkylens do not yield amido-compounds, but part with the nitrogen as ammonia or hydroxylamine.

The varying deportment of the nitro-paraffins with nitrous acid (better NO_2K and H_2SO_4) is very interesting, according as they are derived from primary, secondary or tertiary radicals. (p. 46).

On mixing the primary nitro-compounds (those in which NO_2 is attached to CH_2) with a solution of NO_2K in concentrated potassium hydroxide and adding dilute H_2SO_4, the solution assumes in the beginning an *intense red* color and the **Ethyl-nitrolic acids** are produced. Their structure very probably corresponds to the formula—

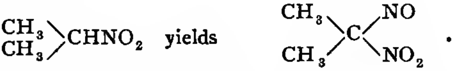


$$CH_3.C\begin{cases}N.OH\\NO_2\end{cases}$$

ethyl nitrolic acid.

The nitrolic acids are colorless crystalline bodies, soluble in ether. They behave like acids. Their alkali salts are dark red in color—hence the appearance, in the beginning, of a red coloration, which disappears in presence of excess of sulphuric acid and reappears on addition of alkali.

The nitro-compounds of the secondary radicals (those in which NO_2 is joined to CH), when exposed to similar treatment, yield a *dark blue* coloration, after which colorless compounds—the **pseudo-nitrols**—separate. These are not turned red by addition of alkali:—

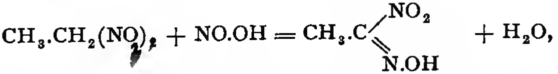


$$\begin{matrix}CH_3\\CH_3\end{matrix}\Big\rangle CHNO_2 \quad \text{yields} \quad \begin{matrix}CH_3\\CH_3\end{matrix}\Big\rangle C\Big\langle\begin{matrix}NO\\NO_2\end{matrix}.$$

In the solid state pseudo nitrols are colorless; when liquid or in solution they are dark blue.

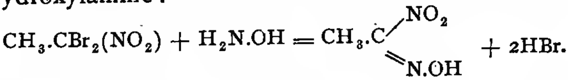
The nitro-compounds of tertiary radicals (like $(CH_3)_3C.NO_2$) do not react with nitrous acid and do not yield colors. Therefore, the preceding reactions serve as a very delicate and characteristic means of distinguishing primary, secondary, and tertiary alcoholic radicals (in their iodides) from each other (secondary nitro-pentane no longer exhibits the reaction). In a similar manner the primary and secondary nitro-derivatives may be detected in a mixture at the same time (*Berichte*, 9, 539, and *Annalen*, 180, 139).

The alkyl-nitrolic acids, produced by the action of nitrous acid (or NO_2K and H_2SO_4) upon the primary nitro-paraffins (see above):—



$$CH_3.CH_2(NO_2) + NO.OH = CH_3.C\begin{cases}NO_2\\N.OH\end{cases} + H_2O,$$

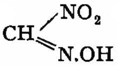
may be prepared synthetically by treating the dibrom nitro-paraffins with hydroxylamine:—

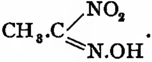


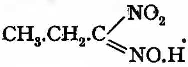
$$CH_3.CBr_2(NO_2) + H_2N.OH = CH_3.C\begin{cases}NO_2\\N.OH\end{cases} + 2HBr.$$

Therefore they are to be regarded as isonitroso- or oximid-compounds (see p. 106).

The nitrolic acids are solid, crystalline, colorless, or faintly-yellow colored bodies, soluble in water, alcohol, ether, and chloroform. They are strong acids, and form salts with alkalies that are not very stable, yielding at the same time a dark red color. They are broken up into hydroxylamine and the corresponding fat acids, by tin and hydrochloric acid. When heated with dilute sulphuric acid they split up into oxides of nitrogen and fatty acids.

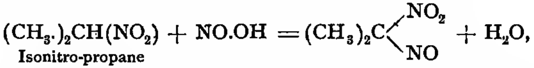
Methyl Nitrolic Acid,  $CH\Big\langle{NO_2 \atop N.OH}$, forms colorless prisms, fusing at 54°. It decomposes into formic acid and nitrogen oxides.

Ethyl Nitrolic Acid,  $CH_3.C\Big\langle{NO_2 \atop N.OH}$. Bright yellow prisms, of sweet taste, melting at 81–82°, and decomposing when covered with concentrated H_2SO_4, into acetic acid and nitrogen oxides.

Propyl Nitrolic Acid,  $CH_3.CH_2.C\Big\langle{NO_2 \atop NO.H}$. Bright yellow prisms, melting at 60°, with decomposition.

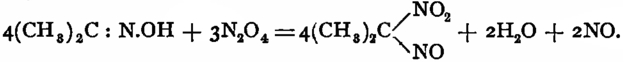
By the action of sodium amalgam upon the alkyl-nitrolic acids, and also upon dinitro-paraffins, the **Leucaurolic acids,** like $(C_2H_4N_2O)_2$, are produced. These probably correspond to the azo-compounds of the benzene group (*Annalen*, 214, 328).

The pseudo-nitrols, isomeric with the nitrolic acids, and formed by the action of nitrous acid upon the secondary nitro-paraffins (see p. 109):—



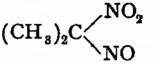
$$\underset{\text{Isonitro-propane}}{(CH_3.)_2CH(NO_2)} + NO.OH = (CH_3)_2C\Big\langle{NO_2 \atop NO} + H_2O,$$

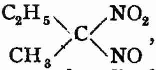
are to be viewed as nitro-nitroso compounds. They are more easily produced by the action of N_2O_4 upon ketonoximes (see these) (*Ber.*, 21, 507):—



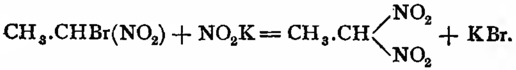
$$4(CH_3)_2C:N.OH + 3N_2O_4 = 4(CH_3)_2C\Big\langle{NO_2 \atop NO} + 2H_2O + 2NO.$$

They are, in all probability, the nitric acid esters of the acetoximes, $(CH_3)_2C = N.O.NO_2$ (*Ber.*, 21, 1294). The pseudo-nitrols are crystalline bodies, colorless in the solid condition, but exhibiting a deep blue color when fused or dissolved (in alcohol, ether, chloroform). They show a neutral reaction, and are insoluble in water, alkalies and acids. Dissolved in glacial acetic acid, they are oxidized by chromic acid to dinitro-compounds.

Propyl Pseudonitrol,  $(CH_3)_2C\Big\langle{NO_2 \atop NO}$, nitro-nitroso-propane, is a white powder, crystallizing from alcohol in colorless, brilliant prisms. It melts at 76°, to a dark blue liquid, and decomposes into oxides of nitrogen and dinitropropane. Chromic acid changes it to β-dinitropropane and acetone.

Butyl Pseudonitrol,  $\begin{matrix}C_2H_5\\CH_3\end{matrix}\!\!>\!C\!<\!\!\begin{matrix}NO_2\\NO\end{matrix}$, is a colorless, crystalline mass, melting at 58°. In its fused state, or when dissolved, it exhibits a deep blue color.

The *dinitro-derivatives* of the paraffins are obtained by the oxidation of the pseudo-nitrols, and by the action of KNO_2, upon the monobrom-derivatives of the nitro-paraffins:—



$$CH_3.CHBr(NO_2) + NO_2K = CH_3.CH\!<\!\!\begin{matrix}NO_2\\NO_2\end{matrix} + KBr.$$

They also result from the acetones by action of concentrated HNO_3. Thus from diethyl ketone, $(C_2H_5)_2CO$, we get dinitroethane, from *α*-dipropyl ketone, $(C_3H_7)_2CO$, *α*-dinitropropane, etc. Methyl-propyl ketone yields *α*-dinitro-propane (*Ber.*, 15, Ref. 56).

They are also produced in an analogous manner from the alkylized aceto-acetic esters (see these) on warming the latter with HNO_3 (*Berichte*, 15, 1495):—

$$CH_3.CO.C(R)H.CO_2.C_2H_5 \text{ yields } CH_3.CO_2H + C(R)H(NO_2)_2 + CO_2.$$

The secondary alcohols (isopropyl alcohol excepted) yield dinitro-paraffins with nitric acid, sustaining at the same time a decomposition analogous to that of the corresponding ketones (*Ber.*, 18, Ref. 217).

Dinitroethane, $CH_3.CH(NO_2)_2$, from brom-nitroethane, is a colorless oil, of specific gravity 1.35 at 23°. It boils at 185–186°. Tin and hydrochloric acid change it to hydroxylamine, aldehyde and acetic acid. It reacts acid and dissolves in potassium hydroxide, forming $CH_3.CK(NO_2)_2$, which crystallizes in yellow prisms. An oil, $CH_3.CBr(NO_2)_2$, that cannot be distilled, is produced by the action of bromine.

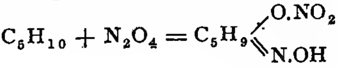
α–**Dinitropropane,** $CH_3.CH_2.CH(NO_2)_2$, from brom-nitropropane, is a colorless oil of specific gravity 1.258 at 22°; it boils at 189°, reacts acid and dissolves in the alkalies, forming salts.

β–**Dinitropropane,** $(CH_3)_2C(NO_2)_2$, is also produced by acting upon isobutyric and isovaleric acids (*Berichte*, 15, 2325) with HNO_3. It forms white camphor-like crystals, fusing at 53° and boiling at 185.5°. It is neutral and insoluble in alkalies. Tin and hydrochloric acid change it to acetone and hydroxylamine.

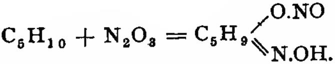
β–**Dinitrobutane,** $CH_3.CH_2.C(NO_2)_2.CH_3$, from butyl pseudo-nitrol, boils at 199° and does not dissolve in alkalies. Hydroxylamine and methyl ethyl ketone are the products it furnishes when acted upon by tin and hydrochloric acid.

Dinitrohexane, $C_6H_{12}(NO_2)_2$, from methyl hexyl carbinol, boils at 212°C.

Nitrosates and *Nitrosites.* These compounds are produced by the action of nitrogen tetroxide and nitrogen trioxide upon the alkylenes:*—



$$C_5H_{10} + N_2O_4 = C_5H_9\!<\!\!\begin{matrix}O.NO_2\\N.OH\end{matrix}$$



$$C_5H_{10} + N_2O_3 = C_5H_9\!<\!\!\begin{matrix}O.NO\\N.OH.\end{matrix}$$

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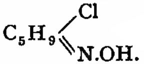
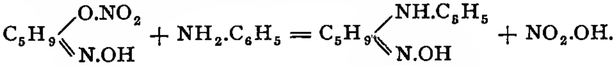
[*] Wallach, *Ann.*, 241, 288; 245, 241; 248, 161. *Ber.*, 20, Ref. 638; 21, Ref. 622.

They contain an iso-nitroso-group, which is also present in the alkyl-nitrolic acids (p. 109), and the ketonoximes (see these). In addition to this the nitrate group ($O.NO_2$), and nitrite group ($O.NO$) are present. In consequence they manifest at the same time the properties of nitric and nitrous acid esters. The nitrosates can be formed by the action of nitric acid and amyl nitrite on the alkylenes (*Ber.*, **21**, Ref. 622). If hydrochloric acid be substituted for nitric acid in this reaction the *Nitroso-chlorides* will result. These contain chlorine instead of the nitrate group, *e.g.*, amylene-nitroso-chloride,  $C_5H_9\Big\langle\begin{matrix}Cl\\N.OH.\end{matrix}$

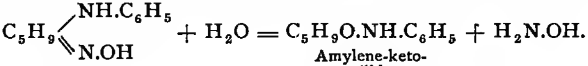
The nitroso-nitrates, or nitrosates, are very reactive, and like the nitric acid esters react so that the nitrate group is replaced. With the amines, such as ethylamine and aniline, they yield the *Nitrolamines*:—



$$C_5H_9\Big\langle\begin{matrix}O.NO_2\\N.OH\end{matrix} + NH_2.C_6H_5 = C_5H_9\Big\langle\begin{matrix}NH.C_6H_5\\N.OH\end{matrix} + NO_2.OH.$$

Amylene-nitrol-aniline.

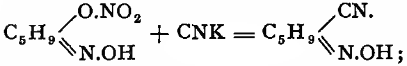
When these are boiled with water the isonitroso-group splits off (similar to the ketonoximes, see same), and is replaced by oxygen, thus giving rise to the *Keto-amines*:—



$$C_5H_9\Big\langle\begin{matrix}NH.C_6H_5\\N.OH\end{matrix} + H_2O = C_5H_9O.NH.C_6H_5 + H_2N.OH.$$

Amylene-keto-anilide.

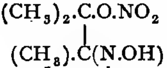
Cyanides (nitriles) result on treating the nitrosates with potassium cyanide:—



$$C_5H_9\Big\langle\begin{matrix}O.NO_2\\N.OH\end{matrix} + CNK = C_5H_9\Big\langle\begin{matrix}CN.\\N.OH;\end{matrix}$$

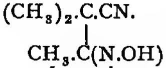
from these the corresponding acids can be obtained.

β-Isoamylene-nitrosate, $C_5H_9(N.OH).O.NO_2$, formed from ordinary amylene (p. 84) (see above and *Ber.*, **22**, Ref. 16), crystallizes in cubes or needles, melting at 97°. Its *Nitro-anilide*, $C_5H_9(N.OH).NH.C_6H_5$, melts at 141°. Potassium cyanide converts the nitrosate into *Isonitrosocyanide*, $C_5H_9(N.OH).CN$, melting at 100°. By saponification of the latter the *acid*, $C_5H_9(N.OH).CO_2H$, is formed. This melts at 97° and suffers further decomposition into CO_2 and $C_5H_{10}(N.OH)$. The latter compound is identical with methyl-isopropyl ketoxime, $(CH_3)_2.CH.C(N.OH).CH_3$. The structure of these derivatives, therefore, corresponds to the following formulas:—



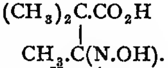
$$\begin{array}{c}(CH_3)_2.C.O.NO_2\\|\\(CH_3).C(N.OH)\end{array}$$

Iso-amylene Nitrosate.



$$\begin{array}{c}(CH_3)_2.C.CN.\\|\\CH_3.C(N.OH)\end{array}$$

Iso-amylene-iso-nitroso-cyanide.



$$\begin{array}{c}(CH_3)_2C.CO_2H\\|\\CH_3.C(N.OH).\end{array}$$

Ketoxime-dimethyl-acetic Acid.

We may note the following among the nitro-compounds, resulting from the action of nitric acid:—

Nitroform, $CH(NO_2)_3$, Trinitromethane, is produced in slight quantity when nitric acid acts upon various carbon compounds. It is most conveniently prepared from trinitro-acetonitrile, $C_2(NO_2)_3N$.

(See this.) When the latter is boiled with water, carbon dioxide is generated, and the ammonium salt of nitroform produced :—

$$\underset{\text{Trinitro-acetonitrile}}{C(NO_2)_3.CN} + 2H_2O = \underset{\text{Ammonium Nitroform.}}{C(NO_2)_3.NH_4} + CO_2.$$

The last is a yellow crystalline compound, from which concentrated sulphuric acid separates free nitroform. This is a colorless, thick oil, solidifying below + 15° to a solid, consisting of cubes. It dissolves rather easily in water, imparting to the latter a yellow color. It explodes when heated rapidly.

Nitroform behaves like a strong acid; the presence of three nitro-groups imparts to hydrogen, in union with carbon, an acid character. Therefore it unites with NH_3 and the alkalies to form salts like $C(NO_2)_3K$, from which acids again liberate nitroform (p. 107). The hydrogen of nitroform can also be replaced by bromine or NO_2.

Brom-nitroform, $C(NO_2)_3Br$, Brom-trinitromethane, is produced by permitting bromine to act for several days upon nitroform exposed to sunlight. The reaction takes place more rapidly by adding bromine to the aqueous solution of the mercury salt of nitroform. In the cold it solidifies to a white crystalline mass, fusing at + 12°. It volatilizes in steam without decomposition.

Tetranitromethane, $C(NO_2)_4$, results on heating nitroform with a mixture of fuming nitric acid and sulphuric acid. It is a colorless oil that solidifies to a crystalline mass, fusing at 13°. It is insoluble in water, but dissolves readily in alcohol and ether. It is very stable, and does not explode on application of heat, but distils at 126° without sustaining any decomposition.

Nitrochloroform, $C(NO_2)Cl_3$—Chloropicrin, trichlor-nitromethane, is frequently produced in the action of nitric acid upon chlorinated carbon compounds (chloral), and also when chlorine or bleaching powder acts upon nitro-derivatives (fulminating mercury, picric acid and nitromethane).

In the preparation of chloropicrin, 10 parts of freshly prepared bleaching powder are mixed to a thick paste with cold water and placed in a retort. To this is added a saturated solution of picric acid, heated to 30°. Usually the reaction occurs without any additional heat, and the chloropicrin distils over with the aqueous vapor (*Annalen*, 139, 111).

Chloropicrin is a colorless liquid, boiling at 112°, and having a specific gravity of 1.692 at 0°. It possesses a very penetrating odor that attacks the eyes powerfully. It explodes when rapidly heated. When treated with acetic acid and iron filings it is converted into methylamine :—

$$CCl_3(NO_2) + 6H_2 = CH_3.NH_2 + 3HCl + 2H_2O.$$

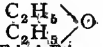
Bromopicrin, $CBr_3(NO_2)$—Tribrom-nitromethane, is formed, like the preceding chloro-compound by heating picric acid with calcium hypobromite (calcium hydroxide and bromine), or by heating nitromethane with bromine (p. 108). It closely resembles chloropicrin and becomes crystalline below + 10°. It can be distilled in a vacuum without decomposition.

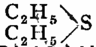
ALCOHOLS, ACIDS AND THEIR DERIVATIVES.

All organic compounds are derived from the hydrocarbons, the simplest derivatives of carbon, by the replacement of the hydrogen atoms by other atoms or atomic groups. The different groups of chemical bodies are characterized in their specific properties by the presence of such substituting side-groups. Thus the alcohols contain OH, the aldehydes CHO, the acids COOH, etc., etc.

In the following pages we will consider the carbon compounds according to the number of side groups yet capable of replacement—as monovalent, divalent, trivalent, etc., compounds. To each of these groups other derivatives are attached bearing intimate genetic connection with them.

By the replacement of one atom of hydrogen of the hydrocarbons by the hydroxyl group OH we get the **monovalent** (monohydric) **alcohols**, *e. g.* $C_2H_5.OH$, in which the H of OH is capable of further exchange. The thio-alcohols or mercaptans, *e. g.* ethyl mercaptan, $C_2H_5.SH$, are analogous to these. **Ethers** result from the union of two monovalent alcohol radicals through the agency of an oxygen atom; corresponding to those are the thio-ethers or sulphur alkyls:—


$$\left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\rangle O$$
Ethyl Ether.

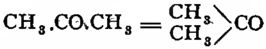

$$\left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\rangle S$$
Ethyl Sulphide.

The **Amines**, $C_2H_5.NH_2$, **Phosphines** and the so-called **metallo-organic compounds** are also derivatives of the alcohol radicals.

When two hydrogen atoms of a methyl group, CH_3, of the hydrocarbons are replaced by one oxygen atom the **aldehydes** result. These are easily obtained from the alcohols by oxidation:—

$$\underset{\text{Ethyl Alcohol.}}{CH_3.CH_2.OH} + O = \underset{\text{Acetaldehyde.}}{CH_3.CHO} + H_2O.$$

The group CHO (aldehyde group) is characteristic of aldehydes. The **ketones** are compounds in which two hydrogen atoms of an intermediate carbon atom (see p. 40) are replaced by one atom of oxygen:—


$$CH_3.CO.CH_3 = \left.\begin{matrix}CH_3\\CH_3\end{matrix}\right\rangle CO \quad \text{Dimethyl-ketone.}$$

They are characterized by the group CO, united to two alkyls.

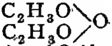
When the two hydrogen atoms attached to the carbon carrying OH are replaced by oxygen, we obtain the **monobasic acids**:—

$$\begin{matrix} CH_3 & & CH_3 \\ | & \text{yields} & | \\ CH_2.OH & & CO.OH \end{matrix}$$

Ethyl Alcohol. Acetic Acid.

The **carboxyl** group—CO.OH—is characteristic of organic acids. The hydrogen atom present in it may be readily replaced by metals, giving rise to salts. Or, the acids may be viewed as compounds of OH with residual atomic groups (*e. g.* $CH_3.CO = C_2H_3O$, acetyl) designated **acid radicals.** The latter, like the alcoholic radicals, are capable of entering into further combinations:—

$C_2H_3O.Cl$
Acetyl Chloride.



$$\begin{matrix} C_2H_3O \\ C_2H_3O \end{matrix}\Big\rangle O$$

Acetyl Oxide.

$C_2H_3O.NH_2$
Acetyl Amide.

The following formulas exhibit the connection between alcohols, aldehydes (or ketones) and acids:—

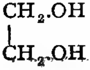
C_2H_6O
Alcohol.

C_2H_4O
Aldehyde.

$C_2H_4O_2$
Acid.

The unsaturated hydrocarbons also yield *unsaturated* alcohols, aldehydes, acids, etc.

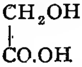
The dihydric alcohols, known as *glycols*, are formed when two hydrogen atoms of the hydrocarbons are replaced by hydroxyl:—



$$\begin{matrix} CH_2.OH \\ | \\ CH_2.OH \end{matrix}$$

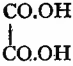
Ethylene Glycol.

In these, four hydrogen atoms can be replaced by oxygen, giving rise to the dihydric *monobasic* and the dihydric *dibasic* acids:—



$$\begin{matrix} CH_2OH \\ | \\ CO.OH \end{matrix}$$

Dihydric Monobasic Acid.



$$\begin{matrix} CO.OH \\ | \\ CO.OH \end{matrix}$$

Dibasic Acid.

The number of CO.OH groups in the acids determines their basicity. The number of hydroxyl groups present is indicated by the terms mono-*valent*, di-*valent*, etc. In the same manner, trivalent (trihydric), mono-, di- and tri-basic acids, etc., are derived from the trivalent alcohols.

The relations of the alcohols and acids to each other, with reference to their valence and basicity, is manifest from the following table:—

	ALCOHOLS.	ACIDS.		
		1-basic.	2-basic.	3-basic
Monovalent.	$CH_3.OH$ Methyl Alcohol.	$CHO.OH$ Formic Acid.		
	$C_2H_5.OH$ Ethyl Alcohol.	$CH_3.COOH$ Acetic Acid.		
Divalent.	$CH_2.OH$ $\vert$ $CH_2.OH$ Ethylene Glycol.	$CH_2.OH$ $\vert$ $CO.OH$ Glycollic Acid.	$CO.OH$ $\vert$ $CO.OH$ Oxalic Acid.	
	$C_3H_6(OH)_2$ Propylene Glycol.	$C_2H_4<\begin{smallmatrix}OH\\CO.OH\end{smallmatrix}$ Lactic Acid.	$CH_2<\begin{smallmatrix}CO.OH\\CO.OH\end{smallmatrix}$ Malonic Acid.	
Trivalent.	$CH_2.OH$ $\vert$ $CH.OH$ $\vert$ $CH_2.OH$ Glycerine.	$CH_2.OH$ $\vert$ $CH.OH$ $\vert$ $CO.OH$ Glyceric Acid.	$CO.OH$ $\vert$ $CH.OH$ $\vert$ $CO.OH$ Oxymalonic Acid.	$C_3H_5\begin{cases}CO_2H\\CO_2H\\CO_2H\end{cases}$ Tricarballylic Acid.
Tetra-valent.	$C_4H_6.(OH)_4$ Erythrite.	$C_4H_4O.(OH)_4$ Erythric Acid.	$C_4H_2O_2.(OH)_4$ Tartaric Acid.	$C_6H_4O_3.(OH)_4$ Citric Acid.
Hexa-valent.	$C_6H_8.(OH)_6$ Mannite.	$C_6H_6O.(OH)_6$ Mannitic Acid.	$C_6H_4O_2.(OH)_6$ Mucic Acid.	

MONOVALENT COMPOUNDS.

MONOVALENT ALCOHOLS.

MONOHYDRIC ALCOHOLS.

The monovalent alcohols contain one hydroxyl group, OH; bivalent oxygen links the monovalent alcohol radical to hydrogen: $CH_3.O.H$, methyl alcohol. This hydrogen atom is characterized by its ability, in the action of acids upon alcohol, to exchange itself for acid residues, forming compound ethers or *esters*, corresponding to the salts of mineral acids:—

$$\underset{\text{Ethyl Alcohol.}}{C_2H_5.OH} + NO_2.OH = \underset{\substack{\text{Ethyl Nitrate or}\\\text{Nitric Ethyl Ester.}}}{C_2H_5.O.NO_2} + H_2O.$$

Alkyls and metals can also replace the hydrogen in alcohol:—

$$\underset{\text{Ethyl-methyl Ether.}}{C_2H_5.O.CH_3} \qquad \underset{\text{Sodium Ethylate.}}{C_2H_5.ONa.}$$

Structure of the Monovalent Alcohols.—The possible isomeric alcohols may be readily derived from the hydrocarbons; they correspond to the mono-halogen isomerides (p. 43). There is one possible structure for the first two members of the normal alcohols:—

$CH_3.OH$ Methyl Alcohol. $C_2H_5.OH.$ Ethyl Alcohol.

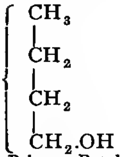
Two isomerides can be obtained from propane, $C_3H_8 = CH_3.CH_2.CH_3$:—

$CH_3.CH_2.CH_2.OH$ and $CH_3.CH(OH).CH_3.$
Propyl Alcohol. Isopropyl Alcohol.

Two isomerides correspond to the formula C_4H_{10} (p. 74):—

$CH_3.CH_2.CH_2.CH_3$ and $CH(CH_3)_3.$
Normal Butane. Isobutane.

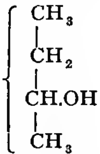
Two isomeric alcohols may be obtained from each of these:—



$$\left\{\begin{array}{l}CH_3\\|\\CH_2\\|\\CH_2\\|\\CH_2.OH\end{array}\right.$$

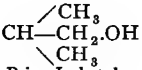
Primary Butyl Alcohol.

and



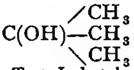
$$\left\{\begin{array}{l}CH_3\\|\\CH_2\\|\\CH.OH\\|\\CH_3\end{array}\right.$$

Secondary Butyl Alcohol.



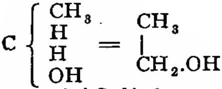
Prim. Isobutyl Alcohol.

and



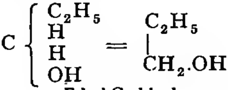
Tert. Isobutyl Alcohol.

The following is a very good method of formulating the alcohols. They are considered as derivatives of methyl alcohol or *carbinol*, $CH_3.OH$. By the replacement of one hydrogen atom in carbinol by alkyls (p. 46) the *primary alcohols* result:—



$$C\left\{\begin{array}{l}CH_3\\H\\H\\OH\end{array}\right. = \begin{array}{l}CH_3\\|\\CH_2.OH\end{array}$$

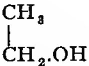
Methyl Carbinol, or Ethyl Alcohol.



$$C\left\{\begin{array}{l}C_2H_5\\H\\H\\OH\end{array}\right. = \begin{array}{l}C_2H_5\\|\\CH_2.OH\end{array}$$

Ethyl Carbinol, or Propyl Alcohol.

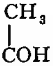
If the replacing group possesses normal structure, the primary alcohols are said to be *normal.* In alcohols of this class the carbon atom carrying the hydroxyl group has two additional hydrogen atoms. Hence compounds of this variety may very easily pass into aldehydes (with group COH) and acids (with COOH group) on oxidation (see p. 114):—



$$\begin{array}{l}CH_3\\|\\CH_2.OH\end{array}$$

Primary Alcohol.

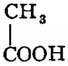
yields



$$\begin{array}{l}CH_3\\|\\COH\end{array}$$

Aldehyde.

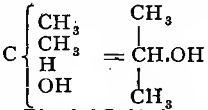
and



$$\begin{array}{l}CH_3\\|\\COOH\end{array}$$

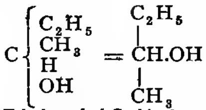
Acid.

The *secondary alcohols* result when two hydrogen atoms in carbinol, $CH_3.OH$, are replaced by alkyls:—



$$C\left\{\begin{array}{l}CH_3\\CH_3\\H\\OH\end{array}\right. = \begin{array}{c}CH_3\\|\\CH.OH\\|\\CH_3\end{array}$$

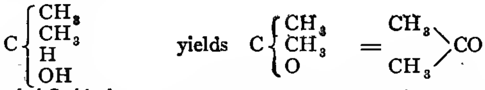
Dimethyl Carbinol, or Isopropyl Alcohol.



$$C\left\{\begin{array}{l}C_2H_5\\CH_3\\H\\OH\end{array}\right. = \begin{array}{c}C_2H_5\\|\\CH.OH\\|\\CH_3\end{array}$$

Ethyl-methyl Carbinol, or Isobutyl Alcohol.

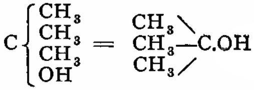
In alcohols of this class the carbon atom carrying the OH group has but one additional hydrogen atom. They do not furnish corresponding aldehydes and acids. When oxidized they pass into ketones (p. 114):—



$$C\left\{\begin{array}{l}CH_3\\CH_3\\H\\OH\end{array}\right. \text{ yields } C\left\{\begin{array}{l}CH_3\\CH_3\\O\end{array}\right. = \begin{array}{l}CH_3\diagdown\\ \qquad\quad CO\\CH_3\diagup\end{array}$$

Dimethyl Carbinol. Acetone.

When, finally, all three hydrogen atoms in carbinol are replaced by alkyls, we get the *tertiary alcohols*:—



$$C\left\{\begin{array}{l}CH_3\\CH_3\\CH_3\\OH\end{array}\right. = \begin{array}{l}CH_3\diagdown\\CH_3—C.OH\\CH_3\diagup\end{array}$$

Trimethyl Carbinol.

These are not capable of forming corresponding aldehydes, acids or ketones. Under the influence of strong oxidizing agents they suffer a decomposition; and acids having a less number of carbon atoms result.

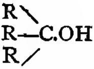
Primary alcohols, therefore, contain the group $CH_2.OH$ joined to *one* alcohol radical (in methyl alcohol it is linked to H); the group CH.OH linked to two alkyls is peculiar to secondary alcohols; while in tertiary alcohols the C in combination with OH has three alkyls attached to it:—

$R.CH_2.OH$

Primary Alcohols.

$$\begin{array}{l}R\diagdown\\ \quad CH.OH\\R\diagup\end{array}$$

Secondary Alcohols.



$$\begin{array}{l}R\diagdown\\R—C.OH\\R\diagup\end{array}$$

Tertiary Alcohols.

The secondary and tertiary alcohols, in distinction from the primary or true alcohols, are designated **pseudo-alcohols.** They are capable of forming esters (p. 116).

Formation of Alcohols.—The most important methods of preparing the monohydric alcohols are the following:—

(1) The replacement of the halogen of monosubstituted hydrocarbons by hydroxyl. This is most easily effected by the action of

freshly precipitated, moist silver oxide. It acts in this instance like a hydroxide :—

$$C_2H_5I + AgOH = C_2H_5.OH + AgI.$$

In many cases the change is best brought about by heating the halogen derivatives with lead oxide and water; the formation of alkylens is avoided in this way. The iodides are more reactive than the chlorides or bromides. Even heating with water alone at high temperatures causes a partial transposition of halogen into hydroxyl derivatives. The halogen derivatives of the secondary and tertiary radicals are very reactive. If heated for some time with 10–15 volumes of water to 100° they are completely converted into alcohols (*Annalen*, 186, 390).

Water at ordinary temperatures converts the tertiary alkyl iodides into alcohols. Heated to 100° with methyl alcohol they pass into alcohols and methyl iodide (*Annalen*, 220, 158).

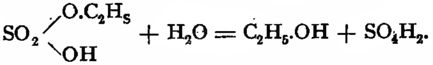
It is often more practical to first convert the halogen derivatives into acetic acid esters, by heating with silver or potassium acetate :—

$$C_2H_5Br + \underset{\text{Potassium Acetate.}}{C_2H_3O.OK} = \underset{\text{Ethyl Acetic Ester.}}{C_2H_5.O.C_2H_3O} + KBr;$$

and then boil these with potassium or sodium hydroxide (saponification), and obtain the alcohols :—

$$C_2H_5.O.C_2H_8O + KOH = C_2H_5.OH + C_2H_8O.OK.$$

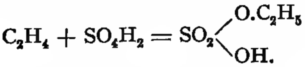
(2) By decomposing the acid esters of sulphuric acid with boiling water :—



$$SO_2\begin{cases} O.C_2H_5 \\ OH \end{cases} + H_2O = C_2H_5.OH + SO_4H_2.$$

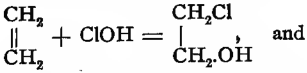
Ethyl Sulphuric Acid.

These esters may be easily obtained by directly combining the unsaturated hydrocarbons with sulphuric acid (see p. 81) :—



$$C_2H_4 + SO_4H_2 = SO_2\begin{cases} O.C_2H_5 \\ OH. \end{cases}$$

A like conversion of unsaturated hydrocarbons is attained by means of hypochlorous acid ; the chlorine derivatives first produced are further changed by nascent hydrogen :—



$$\begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix} + ClOH = \begin{matrix} CH_2Cl \\ | \\ CH_2.OH \end{matrix}, \quad \text{and}$$

$$C_2H_4Cl.OH + H_2 = C_2H_5.OH + HCl.$$

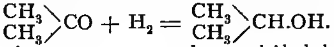
Many alkylens (like iso- and pseudo-butylene) dissolve at once in dilute nitric acid, absorb water, and yield alcohols (*Annalen*, 180, 245).

(3) By acting on the aldehydes and ketones with nascent

hydrogen. The former yields primary, and the latter secondary alcohols (compare p. 118):—

$$CH_3.CH_2.CHO + H_2 = CH_3\,CH_2.CH_2.OH,$$

Propyl Aldehyde. Propyl Alcohol.



$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CO + H_2 = \begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CH.OH.$$

Acetone. Isopropyl Alcohol.

Sodium amalgam in presence of dilute sulphuric or acetic acid will effect this reduction. It is, however, best to use iron filings and 50 per cent. acetic acid (Lieben); or zinc dust and glacial acetic acid; the acetic esters are the first products (*Berichte*, 16, 1715).

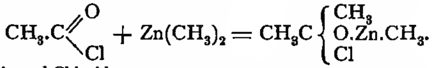
(4) A very remarkable synthetic method, which led to the discovery of the **tertiary** alcohols, consists in the action of the zinc compounds of the alkyls upon the chlorides of the acid radicals. The product is then further changed by the action of water (Butlerow). Thus, from acetyl chloride and zinc methyl, we obtain trimethyl carbinol $(CH_3)_3.C.OH$:—

$$CH_3.COCl \text{ yields } CH_3.C(CH_3)_2.OH.$$

Acetyl Chloride. Trimethyl Carbinol.

The acid chloride (1 molecule) is added, drop by drop, to zinc methyl (2 molecules), cooled with ice, and allowed to remain undisturbed for some hours in the cold, until the mass has become crystalline. After subsequent exposure for two or three days, at ordinary temperatures, the product is decomposed with ice water. Ketones are formed if water be added any sooner (*Annalen*, 188, 121 u. 113).

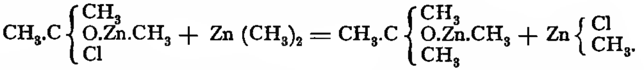
The reaction divides itself into three phases. At first only one molecule of zinc alkyl reacts:—

(1) 

$$CH_3.C\begin{matrix}\nearrow O\\ \searrow Cl\end{matrix} + Zn(CH_3)_2 = CH_3C\begin{cases}CH_3\\O.Zn.CH_3.\\Cl\end{cases}$$

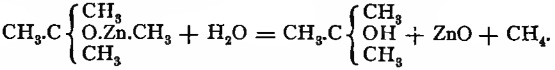
Acetyl Chloride.

The resulting compound gives a crystalline product with the second molecule of the zinc alkyl, and this immediately decomposed with water yields acetone. By longer standing, however, further reaction takes place:—

(2) 

$$CH_3.C\begin{cases}CH_3\\O.Zn.CH_3\\Cl\end{cases} + Zn\,(CH_3)_2 = CH_3.C\begin{cases}CH_3\\O.Zn.CH_3\\CH_3\end{cases} + Zn\begin{cases}Cl\\CH_3.\end{cases}$$

If now water be permitted to take part, a tertiary alcohol will be formed from the first body. The equation is:—

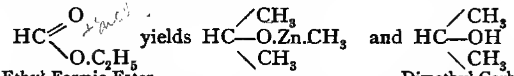


$$CH_3.C\begin{cases}CH_3\\O.Zn.CH_3\\CH_3\end{cases} + H_2O = CH_3.C\begin{cases}CH_3\\OH\\CH_3\end{cases} + ZnO + CH_4.$$

If in the second stage the zinc compound of another radical be employed, the latter may be introduced, and in this manner we obtain tertiary alcohols with two or three different alkyls (*Annalen*, 175, 261, and 188, 110, 122).

It is remarkable that only zinc methyl and ethyl furnish tertiary alcohols, while zinc propyl affords only those of the secondary type. (*Berichte*, 16, 2284.)

(5) Just as we obtained tertiary alcohols from the acid radicals, so can we derive secondary alcohols from the esters of formic acid. Zinc alkyls are allowed to react in this case (or alkyl iodides and zinc), and two alkyls are introduced. At first crystalline intermediate products are produced; these yield the alcohols when treated with water:— 0

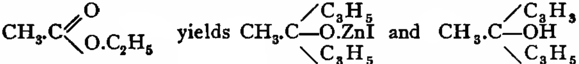


$$HC\begin{cases}O \\ O.C_2H_5\end{cases} \text{ yields } HC\begin{cases}CH_3 \\ O.Zn.CH_3 \\ CH_3\end{cases} \text{ and } HC\begin{cases}CH_3 \\ OH \\ CH_3\end{cases}$$

Ethyl Formic Ester. Dimethyl Carbinol.

Using some other zinc alkyl in the second stage of the reaction, or by working with a mixture of two alkyl iodides and zinc, two different alkyls may also be introduced here (*Annalen*, 175, 362, 374).

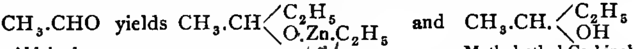
Zinc and allyl iodide (not ethyl-iodide, however) react similarly upon acetic acid esters. Two alkyl groups are introduced and unsaturated tertiary alcohols formed (*Annalen*, 185, 175):—



$$CH_3.C\begin{cases}O \\ O.C_2H_5\end{cases} \text{ yields } CH_3.C\begin{cases}C_3H_5 \\ O.ZnI \\ C_3H_5\end{cases} \text{ and } CH_3.C\begin{cases}C_3H_5 \\ OH \\ C_3H_5\end{cases}$$

Ethyl Acetic Ester. Methyl-diallyl Carbinol.

When zinc alkyls act upon aldehydes, only one alkyl group enters, and the reaction product of the first stage yields a *secondary* alcohol when treated with water. (Compare *Annalen*, 213, 369, and *Berichte*, 14, 2557):—



$$CH_3.CHO \text{ yields } CH_3.CH\begin{cases}C_2H_5 \\ O.Zn.C_2H_5\end{cases} \text{ and } CH_3.CH.\begin{cases}C_2H_5 \\ OH\end{cases}$$

Aldehyde. + HOH Methyl-ethyl Carbinol.

All aldehydes (even those with unsaturated alkyls, and also furfuran) react in this way—but only with zinc methyl and zinc ethyl, while with the higher zinc alkyls the aldehydes suffer reduction to their corresponding alcohols (*Berichte*, 17, Ref. 318). With zinc methyl chloral yields trichlorisopropyl alcohol, $CCl_3.CH(OH).CH_3$; whereas with zinc ethyl it is only reduced to trichlorethyl alcohol (*Annalen*, 223, 162).

The *Ketones* do not react with the zinc alkyls. Even in the action of zinc and ethyl iodide upon such ketones as contain a methyl group, the only result is the splitting-off of water. On the other hand, diethyl-acetone, $(C_2H_5)_2CO$, and dipropyl ketone, $(C_3H_7)_2CO$, are converted by zinc and methyl (ethyl) iodide into zinc alkyl compounds; these, under the influence of water, pass into alcohols (*Berichte*, 19, 60; 24, Ref. 35):—

$(C_2H_5)_2CO$ and zinc ethyl give $(C_2H_5)_3C.OH$.
Propione. Triethyl Carbinol.

$(C_3H_7)_2CO$ and zinc methyl give $(C_3H_7)_2.C(CH_3).OH$.
Butyrone. Dipropyl-methyl Carbinol.

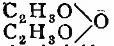
We get unsaturated tertiary alcohols from all the ketones by the action of zinc and allyl iodide (*Annalen*, 196, 113):—

$(CH_3)_2CO$ yields $(CH_3)_2.(C_3H_5).C.OH$.
Dimethyl Ketone. Dimethyl-allyl Carbinol.

(6) By the action of nascent hydrogen upon the chlorides of acid radicals or acid anhydrides:—

$$CH_3.COCl + 2H_2 = CH_3.CH_2.OH + HCl,$$

Acetyl Chloride.



$$\begin{matrix}C_2H_3O \\ C_2H_3O\end{matrix}\!\!>O + 2H_2 = C_2H_5.OH + C_2H_3O.OH.$$

Acetic Acid Anhydride.

Very probably aldehydes are produced at the beginning and are subsequently reduced to alcohols (see p. 121). Primary alcohols alone result by this reaction. Sodium amalgam, or better sodium, serves as the reducing agent. (*Berichte*, 9, 1312.)

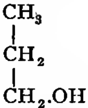
(7) Action of nitrous acid upon the primary amines:—

$$C_2H_5.NH_2 + NO.OH = C_2H_5.OH + N_2 + H_2O.$$

Very often transpositions occur with the higher alkyl-amines and instead of the primary we obtain secondary alcohols. (Compare *Berichte*, 16, 744.)

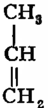
In addition to the above universal methods, alcohols are formed by various other reactions. Their formation in the alcoholic fermentation of sugars in the presence of ferments is of great practical importance. Appreciable quantities of methyl alcohol are produced in the dry distillation of wood. Many alcohols, too, exist, as already formed natural products in compounds, chiefly as compound ethers of organic acids.

Conversion of Primary into Secondary and Tertiary Alcohols. By the elimination of water the primary alcohols become unsaturated hydrocarbons C_nH_{2n} (p. 79). The latter, treated with concentrated HI, yield iodides of secondary alcoholic radicals, as iodine does not attach itself to the terminal but to the less hydrogenized carbon atom (p. 93). Secondary alcohols appear when these iodides are acted upon with silver oxide. The successive conversion is illustrated in the following formulas:—



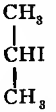
$$\begin{matrix}CH_3 \\ | \\ CH_2 \\ | \\ CH_2.OH\end{matrix}$$

Propyl Alcohol.



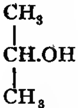
$$\begin{matrix}CH_3 \\ | \\ CH \\ \| \\ CH_2\end{matrix}$$

Propylene.



$$\begin{matrix}CH_3 \\ | \\ CHI \\ | \\ CH_3\end{matrix}$$

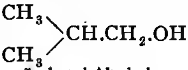
Isopropyl Iodide.



$$\begin{matrix}CH_3 \\ | \\ CH.OH \\ | \\ CH_3\end{matrix}$$

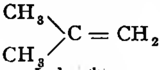
Isopropyl Alcohol.

Primary alcohols in which the group $CH_2.OH$ is joined to a secondary radical, pass in the same manner into tertiary alcohols:—



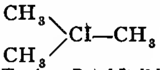
$$\begin{matrix}CH_3 \\ CH_3\end{matrix}\!\!>CH.CH_2.OH$$

Isobutyl Alcohol.



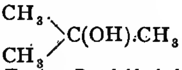
$$\begin{matrix}CH_3 \\ CH_3\end{matrix}\!\!>C = CH_2$$

Isobutylene.



$$\begin{matrix}CH_3 \\ CH_3\end{matrix}\!\!>CI—CH_3$$

Tertiary Butyl Iodide.

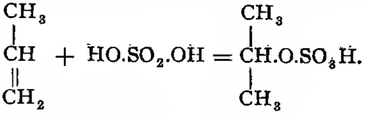


$$\begin{matrix}CH_3 \\ CH_3\end{matrix}\!\!>C(OH).CH_3$$

Tertiary Butyl Alcohol.

The change is better effected by the aid of sulphuric acid.

The sulphuric esters (p. 80), arising from the alkylens, have the sulphuric acid residue linked to the carbon atom, with the least number of attached hydrogen atoms:—



$$\begin{array}{l}CH_3\\ |\\ CH\\ \|\\ CH_2\end{array} + HO.SO_2.OH = \begin{array}{l}CH_3\\ |\\ CH.O.SO_3H.\\ |\\ CH_3\end{array}$$

These pass into alcohols when boiled with water.

Properties and Transpositions. The alcohols are neutral, being neither acid nor basic compounds. They resemble the bases, in that by their action with acids they yield esters (compound ethers), which correspond to salts. In this change, the hydrogen atom of the OH group is replaced by an acid radical (p. 116). Na and K can also replace this hydrogen atom, and then we obtain the metallic alcoholates.

In physical properties alcohols exhibit a gradation corresponding to their increase in molecular weight. This is true of other bodies belonging to homologous series. The lower alcohols are mobile liquids, dissolving readily in water, and possessing the characteristic alcohol odor; the intermediate members are more oily, and dissolve with difficulty in water, while the higher are crystalline solids, without odor or taste. They resemble the fats. Their boiling points increase gradually (with similar structure) in proportion to the increase of their molecular weights. This is about 19° for the difference, CH_2. The primary alcohols boil higher (about 5°) than the isomeric secondary, and the latter higher than the tertiary. Here we observe again that the boiling points are lowered with the accumulation of methyl groups (see p. 73). The higher members are not volatile without decomposition. By distillation they partially break up into water and hydrocarbons C_nH_{2n} (p. 80).

Oxidizing agents (K_2CrO_4 and H_2SO_4) convert the primary alcohols first into aldehydes and then into acids; those of secondary form yield ketones, and the tertiary suffer a partial decomposition (p. 118). The three varieties of alcohols may be readily distinguished by converting them into their iodides and then into the nitro-derivatives, which afford characteristic color reactions (p. 109).

Primary and secondary alcohols, heated with acetic acid, yield esters of the latter; the tertiary, on the contrary, lose water and pass into alkylens (*Annalen*, **220**, 165).

The primary alcohols change to their acids when heated with soda-lime:—

$$R.CH_2.OH + NaOH = R.CO_2H + 2H_2.$$

This reaction may be employed for the detection and estimation of this class of alcohols (*Annalen*, **223**, 259).

When the alcohols are heated with the hydrogen haloids, or what is better, with the halogen derivatives of phosphorus, they are transformed into their corresponding halogen compounds (see p. 92):—

$$C_2H_5.OH + HCl = C_2H_5Cl + H_2O,$$
$$C_2H_5.OH + PCl_5 = C_2H_5Cl + POCl_3 + HCl.$$

These derivatives are therefore designated also *halogen esters* of the alcohols.

Hydrogen (nascent) acting on these, causes a change back into the corresponding hydrocarbons.

Other changes of alcohols will be noted later.

---

(1) THE ALCOHOLS, $C_n H_{2n+1}.OH$.

Methyl Alcohol,	CH_4O	$= CH_3.OH.$
Ethyl "	C_2H_6O	$= C_2H_5.OH.$
Propyl Alcohols,	C_3H_8O	$= C_3H_7.OH.$
Butyl "	$C_4H_{10}O$	$= C_4H_9.OH.$
Amyl "	$C_5H_{12}O$	$= C_5H_{11}.OH.$
Hexyl "	$C_6H_{14}O$	$= C_6H_{13}.OH.$
Heptyl "	$C_7H_{16}O$	$= C_7H_{15}.OH$, etc.
Cetyl Alcohol,	$C_{16}H_{34}O$	$= C_{16}H_{33}.OH.$
Ceryl "	$C_{27}H_{56}O$	$= C_{27}H_{55}.OH.$
Melissyl "	$C_{30}H_{62}O$	$= C_{30}H_{61}.OH.$

1. **Methyl Alcohol**, $CH_3.OH$, wood spirit, occurs among the dry distillation products of wood. We find the methyl group in various natural products, and from them it may be eliminated in the form of the above alcohol. Thus methyl alcohol is obtained by boiling wintergreen oil, the methyl ester of salicylic acid, with potassium hydroxide.

Methyl alcohol is a mobile liquid, with spirituous odor, boiling at 66° (the apparent boiling point can vary very much, according to the nature of the vessel), and having a sp. gr. of 0.796 at 20°. It mixes with water, alcohol, and ether. Its aqueous mixtures have a sp. gr. almost like that of mixtures of ethyl alcohol and equal amounts of water.

The aqueous product obtained in the distillation of wood contains methyl alcohol, acetone, acetic acid, methyl acetic ester, and other compounds. It is distilled over burnt lime. The crude wood spirit that results contains acetone as its chief impurity. To remove this add anhydrous calcium chloride. The latter combines with the alcohol to a crystalline compound. This is removed, freed from acetone by distillation, and afterward decomposed by distilling with water. Pure aqueous methyl alcohol passes over; this is dehydrated with lime. To procure it perfectly pure, it is only necessary to break up oxalic methyl ester, or methyl acetic ester, with KOH.

To detect ethyl in methyl alcohol, heat the latter with concentrated H_2SO_4, when acetylene will be formed from the first. Under this treatment, methyl alcohol becomes methyl ether. The amount of methyl alcohol in wood spirit is determined, quantitatively, by converting it into methyl iodide, CH_3I, through the agency of PI_3 (*Berichte*, 9, 1928). We estimate the quantity of acetone by the iodoform reaction (*Berichte*, 12, 1000).

Wood spirit is employed as a source of heat, and as a solvent for gums and resins. It combines directly with $CaCl_2$, to form $CaCl_2.4CH_4O$, crystallizing in brilliant six-sided plates. The alcohol in this salt conducts itself like water of crystallization. Potassium and sodium dissolve in anhydrous alcohol, to form methylates, *e. g.*, $CH_3.ONa$ (see sodium ethylate, p. 126). Barium oxide dissolves in it to yield a crystalline compound ($BaO.2CH_4O$). When methyl alcohol is heated with soda-lime, sodium formate results:—

$$CH_3.OH + NaOH = CHO.ONa + 2H_2.$$

Oxidizing agents and also air, in presence of platinum black, change methyl alcohol to formic aldehyde and formic acid.

2. **Ethyl Alcohol,** $C_2H_5.OH$, may be obtained from ethyl chloride, C_2H_5Cl, and from ethylene, C_2H_4, by the general methods previously described (p. 119). Its formation in the spirituous fermentation of different varieties of sugar *e. g.*, grape sugar, invert sugar, maltose—is practically very important. It is induced by yeast cells, occurs only in dilute aqueous solution at temperatures ranging from 5–30°, and demands the presence of mineral salts (especially phosphates) and nitrogenous substances (compare Fermentation). Alcoholic fermentation may set in under certain conditions, in ripe fruits, even in the absence of yeast. The various sugars, when fermenting, break up principally into ethyl alcohol and carbon dioxide:—

$$\underset{\text{Glucose.}}{C_6H_{12}O_6} = 2C_2HO_6 + 2CO_2.$$

Other compounds, like propyl, butyl and amyl alcohols (the fusel alcohols), glycerol, and succinic acid, are produced in small quantities at the same time.

The crude spirit obtained from the fermented aqueous solution (of the fermented mash) by distillation is further purified on an extensive scale by fractional distillation in a column apparatus (p. 59). The first portion of the distillate contains the more volatile bodies, like aldehyde, acetal and other substances. Next comes a purer spirit, containing 90–96 per cent. alcohol, and after this common spirit, containing the fusel oils. To remove the latter entirely, the spirit, before distillation and after dilution with water, is filtered through ignited wood charcoal, which retains the fusel oils.

To prepare anhydrous alcohol, the rectified spirit (90–95 per cent. alcohol) is distilled with substances having greater attraction for water than alcohol itself. For this purpose calcium chloride, ignited potashes, or, better, caustic lime (*Annalen*, 160, 249), or barium oxide may be employed. Absolute alcohol dissolves barium oxide, assuming a yellow color at the same time. It is soluble without turbidity in a little benzene; when more than three per cent. water is present cloudiness ensues. On adding anhydrous or absolute alcohol to a mixture of very little anthraquinone and some sodium amalgam it becomes dark green in color, but in the presence of traces of water a red coloration appears (*Berichte*, 10, 927). Traces of alcohol in solutions are detected and determined either by oxidation to aldehyde (see this) or by converting it by means of dilute potash and iodine into iodoform (*Berichte*, 13, 1002).

Its conversion into ethyl benzoate, by shaking with benzoyl chloride and sodium hydroxide (*Berichte*, 19, 3218), also answers for this purpose.

Absolutely pure alcohol possesses an agreeable ethereal odor, boils at 78.3°, and has a specific gravity of 0.80625 at 0°, or 0.78945 at 20°. At —90° it is a thick liquid, at —130° it solidifies to a white mass. It absorbs water energetically from the air. When mixed with water a contraction occurs, accompanied by rise of temperature; the maximum is reached when one molecule of alcohol is mixed with three molecules of water, corresponding to the formula, $C_2H_6O + 3H_2O$. The amount of alcohol in aqueous solutions is given either in per cents. by weight (degrees according to Richter) or volume per cents. (degrees according to Tralles).

Alcohol dissolves many mineral salts, the alkalies, hydrocarbons, resins, fatty acids, and almost all the carbon derivatives. The most of the gases are more readily soluble in it than in water; 100 volumes of alcohol dissolve 7 volumes of hydrogen, 25 volumes of oxygen, and 13 volumes of nitrogen.

Ethyl alcohol forms crystalline compounds with some salts, like calcium chloride and magnesium chloride. It plays the rôle of water of crystallization in them.

Potassium and sodium dissolve in it (also in all other alcohols), separating hydrogen from the hydroxyl group and yielding the so-called metallic alcoholates, *e.g.*, $C_2H_5.ONa$. All the alcohol cannot be thus changed; on evaporating the excess, white crystalline compounds, $C_2H_5.ONa$ or $C_2H_5.OK$, having two and three molecules of alcohol, remain. The alcohol does not escape until the compounds are heated to 200°; then the residual alcoholates form a white, voluminous powder. (Consult *Berichte*, 22, 1011, on the preparation of sodium alcoholate.) Excess of water converts them into alcohol and sodium hydroxide. When but little water is employed, the transposition is only partial. Hence the ethylates are also formed in dissolving KOH and NaOH in strong alcohol. Other metallic oxides, *e.g.*, barium oxide, yield similar derivatives. When aluminium and iodine act upon ethyl and other alcohols, aluminium alcoholates, *e.g.*, aluminium ethylate, $Al(OC_2H_5)_3$ result; these can be distilled in vacuo.

Oxidizing agents (MnO_2 and H_2SO_4, chromic acid, platinum black and air) convert ethyl alcohol into acetaldehyde and acetic acid. Nitric acid changes it at 20–30° into glyoxal, glyoxalic acid, glycollic acid and oxalic acid. When acted upon by chlorine and bromine, chloral and bromal ($CCl_3.CHO$ and $CBr_3.CHO$) are produced.

The *mono*-substituted alcohols, $CH_2X.CH_2.OH$, will be described as halogenhydrins under the glycols.

Trichlor-Ethyl Alcohol, $CCl_3.CH_2.OH$, resulting from the action of zinc ethyl upon chloral, consists of white rhombic crystals, fusing at 17.8° and boiling at 151°; specific gravity 1.55 at 23°. It is slightly soluble in water, but readily soluble in alcohol and ether. When oxidized with nitric acid, it yields trichloracetic acid (*Annalen*, 210, 83).

Nitro-Ethyl Alcohol, $CH_2(NO_2).CH_2.OH$, is prepared in a manner similar to those employed for the nitro-paraffins—by the action of silver nitrite upon ethylene-iodhydrin, $CH_2I.CH_2.OH$. It forms an oil miscible with water. It yields a beautiful sodium salt, and is capable of forming azo-dyes (*Berichte*, 21, 3529; *Annalen*, 256, 28).

3. Propyl Alcohols, $C_3H_7.OH$:—

$CH_3.CH_2.CH_2.OH$	$CH_3.CH(OH)—CH_3$.
Propyl Alcohol.	Isopropyl Alcohol.

(1) **Normal Propyl Alcohol**, $CH_3.CH_2.CH_2.OH$, is produced in the fermentation of sugars, etc. It may be obtained from fusel oil by fractional distillation (p. 125). To get it perfectly pure, the corresponding bromide is converted into the acetate, and this broken up by potassium hydroxide. It may be artificially prepared from propyl aldehyde and propionic anhydride by the action of nascent hydrogen (sodium amalgam). It is an agreeable-smelling liquid of specific gravity 0.8044 at 20°, and boiling at 97.4°. The boiling point is very materially affected by slight additions of water, as a hydrate, $C_3H_8O + H_2O$, is formed, which boils at 87°. It is miscible in every proportion with water, but on the addition of calcium chloride and other easily soluble salts, it separates again from its aqueous solution. Hence it is insoluble in a saturated, cold calcium chloride solution, and this distinguishes it from ethyl alcohol.

It passes into propionic aldehyde and propionic acid, under the influence of oxidizing agents. When heated with 5 volumes of H_2SO_4, it yields propylene. Its *chloride* boils at 46.5°, the *bromide* at 71°, the *iodide* at 102° (p. 96).

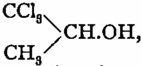
(2) **Secondary or Isopropyl Alcohol**, $(CH_3)_2.CH.OH$, dimethyl carbinol, is prepared from the iso-iodide (p. 96); from acetone $(CH_3)_2.CO$, by the action of sodium amalgam; from acroleïn, C_3H_4O, propylene oxide, C_3H_6O, and dichlorhydrin, $C_3H_5Cl_2.OH$, by means of nascent hydrogen; from glycol iodhydrin, $C_2H_4I.OH$, by action of zinc methyl; from propylamine (p. 122)

by action of nitrous acid, and from formic ester by the aid of zinc and methyl iodide (p. 121).

Preparation.—A mixture of one volume acetone and five volumes of water is shaken with liquid sodium amalgam, and the distillate repeatedly subjected to the same treatment, until an energetic liberation of hydrogen is perceptible. It is then distilled, the distillate dehydrated with ignited potashes and afterwards mixed with pulverized calcium chloride. The resulting crystalline compound is deprived of all adhering acetone by standing over sulphuric acid. If heated, it breaks up into $CaCl_2$ and isopropyl alcohol.

The most practical method of obtaining it is to boil the iodide with ten parts of water and freshly prepared lead hydroxide in a vessel connected with a return condenser, or simply by heating the iodide with twenty volumes of water to 100° (*Annalen*, 186, 391).

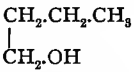
Isopropyl alcohol boils at 82.7°, and has a specific gravity 0.7887 at 20°. It is miscible with water, alcohol and ether; potash will separate it again from the aqueous solution. Oxidizing agents convert it into acetone. Its *chloride*, C_3H_7Cl, boils at 37°, the *bromide* at 60–63°, and the *iodide* at 89° (p. 96). The benzoic ester, $C_3H_7O.C_7H_5O$, breaks up on distillation into benzoic acid and propylene.



Trichlorisopropyl Alcohol, $\begin{matrix}CCl_3\\CH_3\end{matrix}\!>\!CH.OH$, is produced in the action of zinc methyl on chloral. It is crystalline, fuses at 49°, and boils about 155° (*Annalen*, 210, 78).

4. **Butyl Alcohols,** $C_4H_9.OH$. According to theory four isomerides are possible: 2 primary, 1 secondary, and 1 tertiary (p. 117):—

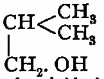
1\.



$$\begin{matrix}CH_2.CH_2.CH_3\\|\\CH_2.OH\end{matrix}$$

Normal Butyl Alcohol.
Propyl Carbinol.

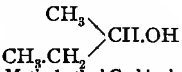
2\.



$$\begin{matrix}CH\!<\!\begin{matrix}CH_3\\CH_3\end{matrix}\\|\\CH_2.OH\end{matrix}$$

Isobutyl Alcohol.
Isopropyl Carbinol.

3\.



$$\begin{matrix}CH_3\\CH_3.CH_2\end{matrix}\!>\!CII.OH$$

Methyl-ethyl Carbinol.

4\. $(CH_3)_3.COH$

Trimethyl Carbinol.

(1) **Normal Butyl Alcohol,** $C_3H_7.CH_2.OH$, forms in the action of sodium amalgam upon normal butyl aldehyde, $C_3H_7.COH$, upon butyryl chloride, $C_3H_7.CO.Cl$, and upon butyric anhydride. It is further produced by a peculiar fermentation of glycerol, brought about in the presence of a schizomycetes (*Berichte*, 16, 1438). It is prepared most readily in this way. It is a liquid with an agreeable odor, has a sp. gr. of 0.8099 at 20° and boils at 116.8°. It is soluble at 22° in 12 volumes of water. Calcium chloride and other salts separate it again from its solution. When oxidized it passes into butyl aldehyde and butyric acid. Its *chloride*, $C_3H_7.CH_2Cl$, boils at 77.6°, the *bromide* at 99.8°, and the *iodide* at 120°.

Trichlorbutyl Alcohol, $CH_3.CHCl.CCl_2.CH_2.OH$, results when zinc ethyl and butyl chloral (see Trichlor-ethyl alcohol, p. 127) are brought together. It crystallizes in prisms, fuses at 62°, and boils under 45 mm. pressure at 120°. If oxidized with nitric acid it yields trichlorbutyric acid (*Annalen*, 213, 374).

(2) **Isobutyl Alcohol,** $C_3H_7.CH_2.OH$, *butyl alcohol of fermentation,* occurs in several fusel oils and especially in the spirit from potatoes. It is a liquid possessing a fusel-oil odor, has a sp. gr. of 0.8020 at 20° and boils at 108.4°. It is soluble in ten parts of water, and is again separated from solution on the addition of salts. When oxidized it affords isobutyric acid. Its *chloride,* C_4H_9Cl, boils at 69°, the *bromide* at 92°, and the *iodide* at 121°. When the bromide is heated to 240° it is converted into tertiary butyl bromide; very probably $(CH_3)_2.C:CH_2$ forms at first, and subsequently yields $(CH_3)_3CBr$ with HBr (p. 94).

When isobutyl alcohol is heated with HCl, HBr or HI there result, in addition to the normal halogen esters, also those of trimethyl carbinol, $(CH_3)_3CX$, because isobutylene, $(CH_3)_2.C:CH_2$, is produced from the former, and this then combines with the halogen hydrides to compounds of the type $(CH_3)_2.CX.CH_3$ (see p. 122).

(3) **Methyl-ethyl Carbinol,** $\begin{matrix}CH_3\\C_2H_5\end{matrix}\!\!>CH.OH$ (Butylene Hydrate), is obtained from its iodide, produced by heating erythrite with hydriodic acid (p. 95); the same iodide is also formed from normal butylene (pp. 84 and 122). The alcohol may further be made by treating formic ester with Zn and CH_3I and C_2H_5I; and from the dichlor-ether, $CH_2Cl.CHCl.O.C_2H_5$, (see Ether) by the action of zinc-ethyl and HI. It is a strongly smelling liquid, boiling at 98°–100°. Its sp. gr. at 0° is 0.827. Heated to 240°–250° it decomposes into water and β-butylene, $CH_3.CH:CH.CH_3$. (Compare *Berichte*, 19, Ref. 610). It yields methyl-ethyl ketone, $\begin{matrix}CH_3\\C_2H_5\end{matrix}\!\!>CO$, when oxidized. Its *iodide* boils at 119–120°.

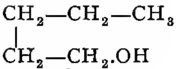
(4) **Trimethyl Carbinol.** $(CH_3)_3.C.OH$, *tertiary* butyl alcohol, is found in small quantities in fusel-oil, and arises in the action of acetyl chloride upon zinc methyl (p. 120). It can also be obtained from the butyl alcohol of fermentation by means of isobutylene (p. 122).

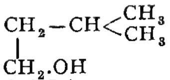
When perfectly anhydrous it crystallizes in rhombic prisms or plates, fusing at 28° and boiling at 83–84°. Its sp. gr. at 30° is 0.7788. It is miscible with water in all proportions, forming the hydrate, $2C_4H_{10}O + H_2O$, which crystallizes in a freezing mixture, and boils at 80°. When oxidized with chromic acid it yields carbon dioxide, acetic acid, acetone, and a little isobutyric acid.

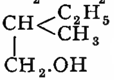
Its *chloride,* C_4H_9Cl, boils at 50–51°, and the *iodide* at 99°. When the latter is heated with zinc and water trimethyl methane, C_3H_{10}, and isobutylene, $C_4H_8 = (CH_3)_2C:CH_2$, result. On combining the latter with ClOH, $(CH_3)_2CCl.CH_2.OH$ will be formed; nascent hydrogen converts this into isobutyl alcohol, $(CH_3)_2.CH.CH_2.OH$.

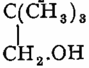
(5) **Amyl Alcohols,** $C_5H_{11}.OH$. Theoretically 8 isomerides are possible: 4 primary alcohols, 3 secondary, and 1 tertiary:—

Primary:

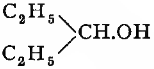
1. 
$$\begin{array}{l} CH_2—CH_2—CH_3 \\ | \\ CH_2—CH_2.OH \end{array}$$

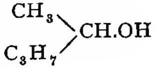
2. 
$$\begin{array}{l} CH_2-CH<^{CH_3}_{CH_3} \\ | \\ CH_2.OH \end{array}$$

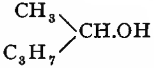
3. 
$$\begin{array}{l} CH<^{C_2H_5}_{CH_3} \\ | \\ CH_2.OH \end{array}$$

4. 
$$\begin{array}{l} C(CH_3)_3 \\ | \\ CH_2.OH \end{array}$$

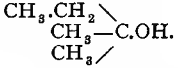
Secondary:

5. 
$$\begin{array}{l} C_2H_5 \diagdown \\ \qquad CH.OH \\ C_2H_5 \diagup \end{array}$$

6. 
$$\begin{array}{l} CH_3 \diagdown \\ \qquad CH.OH \\ C_3H_7 \diagup \end{array}$$

7. 
$$\begin{array}{l} CH_3 \diagdown \\ \qquad CH.OH \\ C_3H_7 \diagup \end{array}$$

Tertiary:

8. 
$$\begin{array}{l} CH_3.CH_2 \diagdown \\ \quad CH_3—C.OH. \\ \quad CH_3 \diagup \end{array}$$

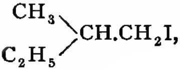
(1) **Normal Amyl Alcohol,** $C_4H_9.CH_2.OH$ (contains the normal butyl group), is obtained from valeraldehyde and from normal pentane. It is most easily prepared from normal amylamine (from caproic acid) by the action of nitrous acid (p. 122, and *Annalen*, 233, 252). It is almost insoluble in water, has a fusel-oil odor, and boils at 137°. Its sp. gr. at 20° equals 0.8168. On oxidation it yields normal valeric acid.

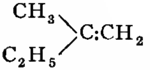
Its *chloride* boils at 106–107° C.; it is produced (together with $C_3H_7.CHCl.CH_3$) in the chlorination of normal pentane. The *bromide* boils at 129°, and the *iodide* at 155.5°

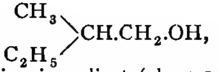
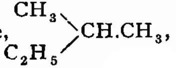
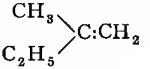
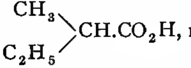
(2) **Isobutyl Carbinol,** $(CH_3)_2CH.CH_2.CH_2.OH$ (Inactive amyl alcohol, isopentyl alcohol), constitutes the chief ingredient of the amyl alcohol of fermentation obtained from fusel oil (p. 125), and occurs as esters of angelic and tiglic acids in Roman camomile oil. It may be obtained in a pure condition by synthesis from isobutyl alcohol, $(CH_3)_2.CH.CH_2.OH$, by converting the latter into the cyanide, the acid, the aldehyde, and finally into the alcohol. It boils at 131.4°, and its sp. gr. at 20° is 0.8104. At 13° it dissolves in 50 parts water. Its *chloride*, $C_5H_{11}Cl$, boils at 100°, the *bromide* at 120.4°, and the *iodide* at 148°. When oxidized it yields inactive valeric acid.

The so-called alcohol of fermentation, possessing a disagreeable odor and boiling at 129–130°, occurs in fusel oil and consists mainly of inactive isobutyl carbinol. In addition, methyl-ethyl carbinol (active amyl alcohol) and probably, too, normal amyl alcohol are present. It rotates the plane of polarization to the left; its activity is due to the presence of active amyl alcohol. The latter distils over first when fusel oil is thus treated.

Fermentation amyl-alcohol, treated with sulphuric acid, yields two amyl-sulphuric acids. The different solubilities and crystalline forms of their barium salts distinguish them. From the more sparingly soluble salt, which forms in rather large quantity, isobutyl carbinol may be obtained by boiling its acid with water. Active amyl alcohol is prepared from the more readily soluble salt. The first alcohol yields inactive valeric acid on oxidation, the second the active acid. A more complete separation of the alcohols is reached by conducting HCl into the mixture. Isobutyl carbinol will be etherified first, the active amyl alcohol remaining (Le Bel) (*Annalen*, 220, 149). When the crude fermentation alcohol is distilled with zinc chloride ordinary amylene is the product. This consists mainly of $(CH_3)_2C{:}CH.CH_3$, resulting from a transposition of isobutyl carbinol; it contains, besides, γ-amylene and α-amylene (compare p. 84). The iodide of the fermentation alcohol is made up principally of $(CH_3)_2.CH.CH_2I$ and


$\left.\begin{array}{l}CH_3\\C_2H_5\end{array}\right\rangle CH.CH_2I$, and yields the amylenes, $(CH_3)_2.CH.CH{:}CH_2$ and

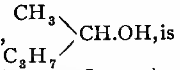

$\left.\begin{array}{l}CH_3\\C_2H_5\end{array}\right\rangle C{:}CH_2$ (p. 85).

(3) **Active Amyl Alcohol,**  $\left.\begin{array}{l}CH_3\\C_2H_5\end{array}\right\rangle CH.CH_2.OH$, secondary butyl carbinol, methyl-ethyl carbinol, is the active ingredient (about 13 per cent.) of the fermentation alcohol, and may be separated from this by the method above described. It boils at 127°. In accordance with its asymmetric structure (p. 63) it is optically inactive and is indeed lævo-rotatory $[\alpha]\,\delta = 4.4°$. Its *chloride*, $C_5H_{11}Cl$, boils from 97–99°, the *bromide* from 117–120°, and the *iodide* from 144–145°. These are all optically active. The same may be noted in regard to ethyl amyl and diamyl obtained from the iodide. Those derivatives, on the contrary, not containing an asymmetric carbon atom, are inactive, *e. g.*, amyl hydride,  $\left.\begin{array}{l}CH_3\\C_2H_5\end{array}\right\rangle CH.CH_3$, and γ-amylene,  $\left.\begin{array}{l}CH_3\\C_2H_5\end{array}\right\rangle C{:}CH_2$ (p. 63 and *Annalen*, 220, 157). Active valeric acid,  $\left.\begin{array}{l}CH_3\\C_2H_5\end{array}\right\rangle CH.CO_2H$, results from the oxidation of active amyl alcohol.

Active amyl alcohol becomes inactive on boiling with NaOH, otherwise it manifests all the properties of the active modification. A mucor will render it again active, but dextro-rotatory (*Berichte*, 15, 1506).

(4) **Tertiary Butyl Carbinol,** $(CH_3)_3.C.CH_2.OH$, has not yet been obtained, but no doubt may be prepared from tertiary butyl alcohol through the cyanide (as in the case of isobutyl carbinol).

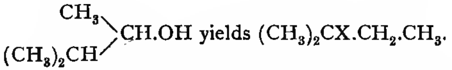
(5) **Diethyl Carbinol,** $(C_2H_5)_2.CH.OH$, is formed by the action of zinc and ethyl iodide upon ethyl formate (p. 121). It boils at 116–117°, and has a specific gravity at 0° of 0.832. Its *iodide* boils at 145°, and the *acetate* at 132°. β-Amylene (p. 84) is obtained from the iodide. *Diethyl ketone*, $(C_2H_5)_2CO$, results from the oxidation of the alcohol. Since *β-amylene*, $C_2H_5.CH{:}CH.CH_3$, yields $C_2H_5.CH_2.CHI.CH_3$ with HI, from which methyl normal propyl carbinol is obtained, we can in this manner convert the diethyl carbinol into the latter alcohol.

(6) **Methyl Normal Propyl Carbinol,**  $\left.\begin{array}{l}CH_3\\C_3H_7\end{array}\right\rangle CH.OH$, is formed from methyl propyl ketone by the action of nascent hydrogen. It may be obtained, too, from the *iodide*, $C_3H_7.CHI.CH_3$ (from α- and β-amylene, see above) and the *chloride* $C_3H_7.CHCl.CH_3$ (from normal pentane). It boils at 118.5°. Its sp. gr. at 0° is 0.824. Its *iodide* boils at 144–145°, and the *chloride* at 103–105°. Methyl

normal propyl ketone is the oxidation product of the alcohol. The *iodide* yields β-amylene.

(7) **Methyl Isopropyl Carbinol,** $\begin{matrix}CH_3\\C_3H_7\end{matrix}\rangle CH.OH$, is obtained by the action of sodium amalgam upon an aqueous solution of the corresponding ketone. It is an oil with a fusel odor, boils at 112.5°, and has a sp. gr. at 0° of 0.833. When oxidized it yields methyl isopropyl ketone.

When acted upon by halogen hydrides and also PCl_5, the derivatives of the type, $\begin{matrix}CH_3\\C_3H_7\end{matrix}\rangle CHX$, do not form, but, in a singular manner, those of tertiary amyl alcohol:—



$$\begin{matrix}CH_3\\(CH_3)_2CH\end{matrix}\rangle CH.OH \text{ yields } (CH_3)_2CX.CH_2.CH_3.$$

Very probably amylene, $(CH_3)_2C{:}CH.CH_3$, is the first product, and this by addition of the halogen hydrides yields the derivatives of tertiary amyl alcohol (compare p. 122).

The real derivatives of methyl-isopropyl-carbinol are obtained from α-isoamylene, $(CH_3)_2.CH.CH{:}CH_2$ (p. 84), by the addition of halogen hydrides at ordinary temperatures or when warmed. The resulting *iodide*, $(CH_3)_2.CH.CHI.CH_3$, boils at 137–139°, the *bromide* at 114–116°, and the *chloride* at 91°. The iodide yields β-isoamylene, $(CH_3)_2C{:}CH.CH_3$.

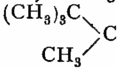
(8) **Tertiary Amyl Alcohol,** $\left.\begin{matrix}(CH_3)_2\\C_2H_5\end{matrix}\right\}C.OH$, Dimethyl-ethyl-carbinol, Amylene hydrate. This is synthetically prepared by the action of zinc methyl on propionyl chloride. It may be obtained from γ-amylene, $\begin{matrix}CH_3\\C_2H_5\end{matrix}\rangle C{:}CH_2$, and β-isoamylene, $(CH_3)_2C{:}CH.CH_3$, when their HI compounds are heated with lead oxide and water. Since ordinary amylene consists chiefly of β-isoamylene (p. 85), tertiary amyl alcohol is most practically prepared from the first by shaking it with sulphuric acid and boiling the solution with water (*Annalen*, 190, 345).

Tertiary amyl alcohol has an odor like that of camphor, boils at 102.5°, solidifies at —12.5° and melts at —12°. Its specific gravity at 0° is 0.827. Its *iodide* boils at 127–128°, the *bromide* at 108–109°, and the *chloride* at 86°. At 200° it decomposes into water and β-isoamylene. Acetic acid and acetone are its oxidation products.

6. **Hexyl and Caproyl Alcohols,** $C_6H_{13}.OH$. Seventeen isomerides are theoretically possible: 8 primary (as there are eight amyl radicals), 6 secondary, and 3 tertiary. Of the eight known at present there may be mentioned:—

(1) **Normal Hexyl Alcohol,** $CH_3.(CH_2)_4.CH_2.OH$. This was first obtained (together with methyl butyl carbinol) from normal hexane. It can be prepared pure from caproic acid, $C_6H_{12}O_2$, by reduction, and by the transformation of hexylamine (from œnanthylic acid, $C_7H_{14}O_2$, *Berichte*, 16, 744). Hexyl butyrate occurs in the volatile products of some *Heracleum* varieties (together with octyl acetate). The alcohol may be obtained from these by saponification with caustic potash. It boils at 157°, and has a specific gravity at 23° of 0.819. Normal caproic acid is its oxidation product. The *iodide*, $C_6H_{13}I$, boils at 180°, and the *chloride*, $C_6H_{13}Cl$, at 130–133°.

(2) **Methyl-tertiary Butyl Carbinol,** $(CH_3)_3.C.CH.OH.CH_3$, Pinacolyl alcohol. Nascent hydrogen acting on pinacoline (see this) produces the above

alcohol. When cooled it crystallizes and melts at +4°. It boils at 120°, and has a specific gravity of 0.834. If oxidized with a chromic acid mixture it first yields the ketone,  $\begin{matrix}(CH_3)_3C\\CH_3\end{matrix}\Big\rangle CO$, *pinacoline*, which afterwards breaks up into carbon dioxide and trimethyl acetic acid.

(3) **Fermentation Hexyl Alcohol or Caproyl Alcohol,** $C_6H_{13}.OH$, is found in the fusel oil of grape spirit. It boils at 150°. Its constitution is not well determined. That it is a primary alcohol is evident from the fact that when it is oxidized it changes to caproic acid.

7. **Heptyl or Œnanthyl Alcohols,** $C_7H_{15}.OH$. Thirteen of the thirty-eight possible isomerides are known. The following may be noticed :—

(1) **Normal Heptyl Alcohol,** $CH_3(CH_2)_5.CH_2.OH$, from œnanthyl aldehyde (*Annalen*, 200, 102) and normal heptane, boils at 175° and yields normal œnanthylic acid on oxidation.

(2) **Dimethyl-tertiary Butyl Carbinol,** $C(CH_3)_3.C(CH_3)_2.OH$, or Pentamethyl-ethyl alcohol, obtained from trichlor-methyl acetic anhydride, $C(CH_3)_3.COCl$, by means of zinc methyl, melts at + 17° and boils at 131–132°. It yields a crystalline hydrate, $2C_7H_{16}O + H_2O$, with water. This melts at 83°. Its *chloride* boils at 136°, and the *iodide* at 141°.

The following higher normal alcohols are known: Octyl, cetyl, ceryl, and melissyl alcohols occur naturally as esters; the others are obtained from the corresponding aldehydes by reduction (p. 120).

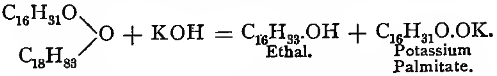
Octyl Alcohol, $C_8H_{18}O$, occurs as octyl acetate in the volatile oil of *Heracleum spondylium*, as butyrate in the oil of *Pastinaca sativa*, and together with hexyl butyrate in the oil from *Heracleum giganteum*. It boils at 190–192°, and at 16° it has a sp. gr. = 0.830. Caprylic acid is its oxidation product.

Decyl Alcohol, $C_{10}H_{21}.OH$, from capric aldehyde, melts at +7°, and under 15 mm. pressure boils at 43.5°.

Dodecatyl Alcohol, $C_{12}H_{25}.OH$, from lauraldehyde, melts at 24°, and boils at 119° under a pressure of 15 mm.

Tetradecatyl Alcohol, $C_{14}H_{29}.OH$, from myrisitaldehyde, melts at 32°, and under a pressure like that given with the preceding compounds boils at 167°.

Cetyl Alcohol, $C_{16}H_{33}.OH$, **Hexadecyl Alcohol,** formerly called *ethal*, is prepared from the cetyl ester of palmitic acid, the chief ingredient of spermaceti, by saponification with alcoholic potash :—



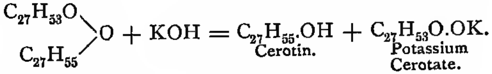
$$\begin{matrix}C_{16}H_{31}O\\C_{18}H_{83}\end{matrix}\Big\rangle O + KOH = \underset{\text{Ethal.}}{C_{16}H_{33}.OH} + \underset{\text{Potassium Palmitate.}}{C_{16}H_{31}O.OK.}$$

It may also be obtained in a pure condition by the reduction of palmitic aldehyde, whereas when prepared from spermaceti it is contaminated with octodecyl alcohol (*Berichte*, 17, 1627).

Ethal is a white, crystalline mass fusing at 49.5°, and distilling about 340° with scarcely any decomposition (under 15 mm. pressure it boils at 189°). It yields, when fused with potassium hydroxide, palmitic acid.

Octodecyl Alcohol, $C_{18}H_{37}.OH$, from stearaldehyde, fuses at 59°, and boils at 210° (under 15 mm.).

Ceryl Alcohol, $C_{27}H_{55}.OH$—*Cerotin*—as ceryl cerotic ester, constitutes Chinese wax. It is obtained by melting the latter with caustic potash:—



$$\left.\begin{array}{l}C_{27}H_{53}O\\C_{27}H_{55}\end{array}\right\rangle O + KOH = \underset{\text{Cerotin.}}{C_{27}H_{55}.OH} + \underset{\text{Potassium Cerotate.}}{C_{27}H_{53}O.OK.}$$

Ceryl alcohol is a white, crystalline mass, fusing at 79°. It yields cerotic acid when fused with potassium hydroxide.

Melissyl Alcohol, $C_{30}H_{61}.OH$, myricyl alcohol, occurs as myricyl palmitate in beeswax. It is isolated in the same manner as the preceding compound, and melts at 85°. Its *chloride* melts at 64°, and the *iodide* at 69.5°.

2. UNSATURATED ALCOHOLS, $C_nH_{2n-1}.OH$.

These are derived from the unsaturated alkylens, C_nH_{2n}, in the same manner as the normal alcohols are obtained from their hydrocarbons. In addition to the general character of alcohols they are also capable of directly binding two additional affinities.

The lowest member of the series—the so-called *vinyl alcohol*—$C_2H_3.OH = CH_2:CH.OH$, appears to exist in ordinary crude ether (*Berichte*, 22, 2000), but cannot be prepared artificially, because in all the reactions in which it should form, the isomeric acetaldehyde, $CH_3.CHO$, is produced. It seems to be the universal rule, that the atomic grouping $= C:CH.OH$, in the act of formation, is transposed into $= CH.CHO$, as aldehydes result instead of the expected secondary alcohols. The group $C.C(OH:CH_2$ (with tertiary alcohol group) passes over into $C.CO.CH_3$, since ketones are always produced (compare acetone).* These facts explain many abnormal reactions (compare *Berichte*, 13, 309, and 14, 320). The same rule holds good for the unsaturated oxy-acids in free condition, but does not apply to their salts and esters (*Berichte*, 16, 2824). When the allyl alcohols are oxidized with potassium permanganate they yield triatomic glycerols (p. 82).

1. Allyl Alcohol, $C_3H_5.OH = CH_2:CH.CH_2.OH$. This may be prepared by heating allyl iodide to 100° (p. 99) with 20 parts water. It is produced, also, when nascent hydrogen acts upon acroleïn, $CH_2:CH.COH$, and sodium upon dichlorhydrin. $CH_2Cl.CHCl.CH_2.OH$. It is best prepared from glycerol by heating the latter with formic or oxalic acid.

Preparation.—A mixture of four parts glycerol and 1 part crystallized oxalic acid, with addition of ½ per cent. ammonium chloride, is slowly heated to 100° in a retort. Carbon dioxide is disengaged, while formic acid and some allyl alcohol

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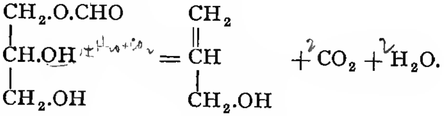
* The two isomeric forms are probably tautomeric (see p. 54).

pass over. When the liberation of gas has ceased somewhat, the heat is raised to 200°, and the distillate collected. The latter contains, besides allyl alcohol, some allyl formate and acrolein. To further purify it the distillation is repeated, the product warmed with KOH and dehydrated by distillation over barium oxide (*Annalen*, 167, 222).

In this reaction the oxalic acid at first breaks up into carbon dioxide and formic acid, which forms an ester with the glycerol; this then decomposes into allyl alcohol, carbon dioxide, and water:—



$$\begin{array}{l}CH_2.O.CHO\\ |\\ CH.OH\\ |\\ CH_2.OH\end{array} = \begin{array}{l}CH_2\\ \|\\ CH\\ |\\ CH_2.OH\end{array} + CO_2 + H_2O.$$

By this method 20–25 per cent. of the glycerol is changed to allyl alcohol.

Allyl alcohol is a mobile liquid with a pungent odor, boiling at 96–97°, and having at 20° a specific gravity of 0.8540. It solidifies at —50°. It is miscible with water and burns with a bright flame. It yields acroleïn and acrylic acid when oxidized with silver oxide, and only formic acid (no acetic) when chromic acid is the oxidizing agent. Nascent hydrogen is apparently without effect upon it; when heated to 150° with KOH formic acid, normal propyl alcohol and other products are obtained.

For the halogen esters of allyl alcohol see page 98.

It combines with Cl_2 and Br_2 to form the β-dichlorhydrins of glycerol (see these). The monosubstituted allyl alcohols are represented by two isomerides:—

CH_2:CCl.CH_2.OH	and	CHCl:CH.CH_2.OH.
α-Chlorallyl Alcohol.		β-Chlorallyl Alcohol.

The first of these is formed from α-dichlorpropylene, CH_2:CCl.CH_2Cl, on boiling with a sodium carbonate solution; it boils at 136°. When it is dissolved in sulphuric acid and distilled with water it becomes acetone alcohol, CH_3.CO.CH_2 OH.

β-**Chlorallyl Alcohol**, from β-dichlorpropylene, CHCl:CH.CH_2Cl, boils at 153°, and causes painful blisters.

β-**Bromallyl Alcohol**, CHBr:CH.CH_2.OH, from β-dibrompropylene, boils at 152°, and yields propargylic alcohol with KOH.

2. **Crotyl Alcohol**, $C_4H_7.OH = CH_3.CH{:}CH.CH_2.OH$, is obtained from crotonaldehyde, CH_3.CH:CH.CHO, by means of nascent hydrogen. It boils at 117–120°.

3. Higher unsaturated alcohols of the allyl series, having tertiary structure, arise in the action of zinc and allyl iodide upon ketones and in the decomposition of the resulting product with water (p. 121).

(3) UNSATURATED ALCOHOLS, C_nH_{2n-3}.OH.

Propargyl Alcohol, $C_3H_4O = CH{:}C.CH_2.OH$, is the only known alcohol of the acetylene series. There is a triple union of two carbon atoms present in this compound. It is produced on heating β-bromallyl alcohol (see above) with potassium hydroxide and water:—

$$CHBr{:}CH.CH_2.OH \text{ yields } CH\vdots C.CH_2.OH.$$

Propargyl alcohol (or propinyl alcohol) is a mobile, agreeable-smelling liquid, with a sp. gr. at 20° of 0.9715. It boils at 114–115°, and dissolves readily in water. With an ammoniacal cuprous chloride solution (p. 87) it forms a yellow precipitate, $(C_3H_2.OH)_2Cu_2$, from which the alcohol is again set free by acid. Silver solutions produce a white precipitate, $C_3H_2Ag.OH$.

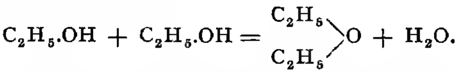
Trichloride of phosphorus converts the alcohol into the *chloride*, C_3H_3Cl. This boils at 65°. The *bromide*, C_3H_3Br, formed by PBr_3, boils at 88–90°; the *iodide* boils at 115°. The *acetate*, $C_3H_3.O.C_2H_3O$, results when acetyl chloride acts upon the alcohol. Its boiling point is 125°.

Ethyl-Propinyl Ether, $C_3H_3.O.C_2H_5$, is made from glyceryl bromide, $C_3H_5Br_3$, and the various dichlor- and dibrom-propylenes, $C_3H_4Br_2$, by the aid of alcoholic potash. It is a liquid with a penetrating odor, of sp. gr. 0.8326 at 20°, and boils at 80°. Its copper compound, $(C_3H_2.O.C_2H_5)_2Cu$, is yellow colored, while that with silver, $C_3H_2Ag.O.C_2H_5$, is white.

Higher alcohols, in which the double union of carbon atoms occurs twice, are produced by the action of zinc and allyl iodide upon ethers of formic acid and even of acetic acid, whereby secondary and tertiary alcohols result (p. 120). These alcohols absorb four bromine atoms, but do not, however, enter into combination with copper and silver. This accords with their structure.

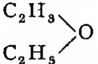
ETHERS.

The oxides of the alcohol radicals are thus designated. In the ethers of the monohydric alcohols two alkyls are present, joined to each other by an oxygen atom. They may be considered also as anhydrides of the alcohols, formed by the elimination of water from two molecules of alcohol:—



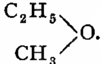
$$C_2H_5.OH + C_2H_5.OH = \begin{matrix}C_2H_5\diagdown\\ \diagup\\ C_2H_5\end{matrix}\!\!O + H_2O.$$

Ethers containing two similar alcohol radicals are termed *simple ethers;* those with different radicals, *mixed ethers*:—



$$\begin{matrix}C_2H_5\diagdown\\ \diagup\\ C_2H_5\end{matrix}\!\!O$$

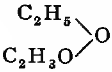
Ethyl Ether, or
Diethyl Ether.



$$\begin{matrix}C_2H_5\diagdown\\ \diagup\\ CH_3\end{matrix}\!\!O.$$

Methyl-ethyl
Ether.

We must make a distinction between the above and the so-called compound ethers or *esters*, in which both an alcohol radical and an acid radical are present, *e. g.*,—



$$\left.\begin{matrix}C_2H_5\\C_2H_3O\end{matrix}\right\rangle O$$ Ethyl Acetic Ester.

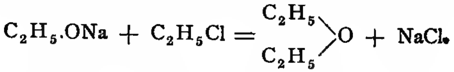
The properties of these are entirely different from those of the alcohol ethers. In the following pages they will always be termed *esters*.

The following are the most important methods of preparing ethers:—

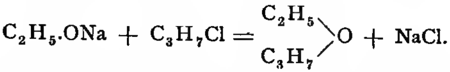
1. Action of the alkylogens upon metallic oxides, especially silver oxide:—

$$2C_2H_5I + Ag_2O = (C_2H_5)_2O + 2AgI.$$

2. The action of the alkylogens upon the sodium alcoholates in alcoholic solution. Mixed ethers are also formed here:—



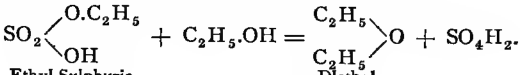
$$C_2H_5.ONa + C_2H_5Cl = \left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\rangle O + NaCl.$$



$$C_2H_5.ONa + C_3H_7Cl = \left.\begin{matrix}C_2H_5\\C_3H_7\end{matrix}\right\rangle O + NaCl.$$

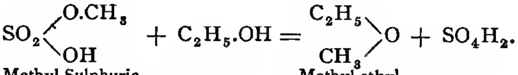
Consult *Berichte*, 22, Ref. 381, upon the speed of these reactions.

3. Heating the sulphuric esters with alcohols:—



$$SO_2\left\langle\begin{matrix}O.C_2H_5\\OH\end{matrix}\right. + C_2H_5.OH = \left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\rangle O + SO_4H_2.$$

Ethyl Sulphuric Acid. Diethyl Ether.



$$SO_2\left\langle\begin{matrix}O.CH_3\\OH\end{matrix}\right. + C_2H_5.OH = \left.\begin{matrix}C_2H_5\\CH_3\end{matrix}\right\rangle O + SO_4H_2.$$

Methyl Sulphuric Acid. Methyl-ethyl Ether.

The formation of ethers by directly heating the alcohols with sulphuric acid is based on this reaction:—

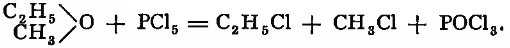
$$2C_2H_5.OH + SO_4H_2 = (C_2H_5)_2O + SO_4H_2 + H_2O.$$

By mixing and warming alcohol with sulphuric acid, a sulphuric ester (together with water) is produced (p. 119). With excess of alcohol, on application of heat, this breaks up into ether and sulphuric acid. The ether and water distil over while the sulphuric acid remains behind. If a new portion of alcohol be added to this residue the process repeats itself. In this way, an unlimited amount of alcohol can be changed to ether by one and the same quantity of sulphuric acid, providing the latter does not sustain a slight and otherwise different transposition. Formerly, when the mechanism of the reaction was yet unexplained, this process was included in the category of *catalytic* actions. The explanation of the etherification process (by Williamson, in 1852) marks an important turning point in the history of chemistry.

When a mixture of two alcohols is permitted to act upon sulphuric acid, three ethers are simultaneously formed; two are simple and one a mixed ether. Other polybasic acids, like phosphoric, arsenic, and boric, behave like sulphuric acid.

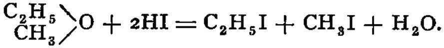
Ethers are neutral, volatile bodies, nearly insoluble in water. The lowest members are liquid; the highest, *e. g.*, cetyl ether, are solids. Their boiling points are very much lower than those of the corresponding alcohols (*Annalen*, 243, 1).

Chemically, ethers are very indifferent, because all the hydrogen is attached to carbon. When oxidized they yield the same products as their alcohols. They yield ethereal salts when heated with concentrated sulphuric acid. Phosphorus chloride converts them into alkyl chlorides:—



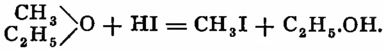
$$\left.\begin{matrix}C_2H_5\\CH_3\end{matrix}\right\rangle O + PCl_5 = C_2H_5Cl + CH_3Cl + POCl_3.$$

The same occurs when they are heated with the haloid acids, especially with HI:—



$$\left.\begin{matrix}C_2H_5\\CH_3\end{matrix}\right\rangle O + 2HI = C_2H_5I + CH_3I + H_2O.$$

When acted upon by HI in the cold, they decompose into alcohol and an iodide. With mixed ethers it is the iodide of the lower radical that is invariably produced (*Berichte*, 9, 852):—



$$\left.\begin{matrix}CH_3\\C_2H_5\end{matrix}\right\rangle O + HI = CH_3I + C_2H_5.OH.$$

Many ethers, especially those with secondary and tertiary alkyls and those with unsaturated alkyls, break up into alcohols (*Berichte*, 10, 1903), when heated with water or dilute sulphuric acid to 150°.

Methyl Ether, $(CH_3)_2O$, is prepared by heating methyl alcohol with sulphuric acid. It is an agreeable-smelling gas, which may be condensed to a liquid at about — 23°. Water dissolves 37 volumes and sulphuric acid upwards of 600 volumes of the gas.

In preparing it 4 parts methyl alcohol and 6 parts concentrated sulphuric acid are heated to 140°, in a flask, in connection with a return condenser. The liberated gas is purified by conducting it through potash. (*Berichte*, 7, 699.)

Substitution products form when chlorine is allowed to act gradually: $CH_2Cl.O.CH_3$ boils at 60°, $(CH_2Cl)_2O$ boils at 105°, and at last perchlormethyl ether, $(CCl_3)_2O$, which decomposes about 100°.

Ethyl Ether, $(C_2H_5)_2O$, is prepared by heating ethyl alcohol with sulphuric acid (p. 137).

A mixture of 5 parts (80–90 per cent.) alcohol and 9 parts H_2SO_4 is warmed in a flask connected with a condenser. A thermometer passes through the cork of the vessel and dips into the liquid. When the temperature has reached 140°, a slow stream of alcohol is allowed to enter the flask through a tube leading into the latter. The temperature given must be maintained. The ethyl sulphuric acid produced at the beginning reacts at 140° upon the entering alcohol forming sulphuric acid and ether, which regularly distils over with the water formed in the reaction. The distillate is a mixture of ether, water, and some alcohol. It is shaken with soda, to combine sulphurous acid, the lighter layer of ether is siphoned off and distilled over lime. There is always some alcohol in the product. To remove this entirely distil repeatedly over sodium, until hydrogen is no longer evolved. Any water in the ether may be detected by shaking the latter with an equal volume of CS_2, when a turbidity will ensue. To detect alcohol, ether is agitated with aniline violet. When the former is absent the ether remains uncolored.

Ethyl ether is a mobile liquid with peculiar odor and specific gravity at 0° of 0.736. When anhydrous, it does not congeal at — 80°. It boils at 35° and evaporates very rapidly even at medium temperatures. It dissolves in 10 parts water and is miscible with alcohol. Nearly all the carbon compounds insoluble in water, such as the fats and resins, are soluble in ether. It is extremely inflammable, burning with a luminous flame. Its vapor forms a highly explosive mixture with air. When inhaled, ether vapor brings about unconsciousness. *Hoffmann's Anodyne* is a mixture of 3 parts alcohol and 1 part ether.

Ether unites with bromine to form peculiar, crystalline addition products, somewhat like bromine hydrate; it combines, too, with water and metallic salts. When heated with water and sulphuric acid to 180° ethyl alcohol results. Chlorine acting upon cooled ether forms various substitution products: monochlorether, $CH_3.CHCl.O.C_2H_5$, boiling point 98°, dichlorethyl oxide, $CH_2Cl.CHCl.O.C_2H_5$, boiling point 145°, and higher derivatives. An isomeric dichlorether, $(CH_3.CH.Cl)_2O$, is produced when HCl acts upon aldehyde. It boils at 116°. *Perchlorinated Ether*, $(C_2Cl_5)_2O$, the last product of the action of chlorine on ethyl oxide, is a crystalline body, fusing at 68° and decomposing upon distillation into C_2Cl_6 and trichloracetyl chloride, $C_2Cl_3O.Cl$.

When ozone is conducted into anhydrous ether, a thick liquid, having the composition $C_8H_{20}O_3$, is formed. This explodes on being heated. It is considered an ethyl peroxide, $(C_2H_5)_4O_3$. Water converts it into alcohol and hydrogen peroxide.

Methyl Ethyl Ether, $CH_3.O.C_2H_5$, boils at 11°. **Methyl Propyl Ether**, $CH_3.O.C_3H_7$, at 50°.

Normal Propyl Ether, $(C_3H_7)_2O$, boils at 86°. **Isopropyl Ether**, from isopropyl iodide, boils at 60–62°.

Isoamyl Ether, $(C_5H_{11})_2O$, is formed together with amylene, and its polymerides when fermentation amyl alcohol is heated with sulphuric acid. It boils at 176°, and has a specific gravity of 0.779.

Cetyl Ether, $(C_{16}H_{33})_2O$, from cetyl iodide, crystallizes from ether in brilliant leaflets, fuses at 55°, and boils at 300°.

Vinyl Ether, $(C_2H_3)_2O$, is obtained from vinyl sulphide by the action of dry silver oxide. It boils at 39°.

Allyl Ether, $(C_3H_5)_2O$, from allyl iodide, boils at 85°.

Vinyl Ethyl Ether, $C_2H_3.O.C_2H_5$, is produced when chloracetal, $CH_2Cl.CH.(O.C_2H_5)_2$ (obtained from acetal by chlorination and from dichlor-ether, $CH_2Cl.CHCl.O.C_2H_5$, by aid of sodium alcoholate), is heated with sodium. It is a liquid with an allyl-like odor, and boils at 35.5°. The addition of chlorine changes it again to dichlorether. When boiled with dilute sulphuric acid it decomposes into ethyl alcohol and aldehyde (p. 134).

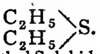
Allyl Ethyl Ether, $C_3H_5.O.C_2H_5$, from allyl iodide and sodium ethylate, boils at 66°. It combines directly with Br_2, Cl_2 and $ClOH$.

MERCAPTANS AND THIO-ETHERS.

The sulphur analogues of the alcohols and ethers are the *thio-alcohols* or *mercaptans* and *thio-ethers* or *alkyl-sulphides* :—

$C_2H_5.SH$

Ethyl Hydrosulphide.



$$\left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right>S.$$

Ethyl Sulphide.

Although they closely resemble the alcohols and ethers in general, the sulphur in them imparts additional specific properties. In the alcohols the H of OH is replaceable by alkali metals almost exclusively; in the mercaptans it can also be replaced by heavy metals (by action of metallic oxides). The mercaptans react very readily with mercuric oxide, to form crystalline compounds :—

$$2C_2H_5.SH + HgO = (C_2H_5.S)_2Hg + H_2O.$$

Hence their designation as mercaptans (from *Mercurium captans*).

The methods resorted to for their formation are perfectly analogous to those employed for the alcohols. They are produced :—

(1) By the action of the alkylogens upon potassium sulphydrate in alcoholic solution :—

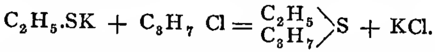
$$C_2H_5Cl + KSH = C_2H_5.SH + KCl.$$

Similarly, the thio-ethers are formed by action of the alkylogens upon potassium sulphide :—

$$2C_2H_5Cl + K_2S = (C_2H_5)_2S + 2KCl.$$

When polysulphides are employed instead of K_2S, polysulphides of the alcohol radicals, like $\left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}S_2$, are obtained.
Ethyl Disulphide.

The alkyl sulphides are also produced when the alkylogens act upon the metallic compounds of the mercaptans. Mixed thio-ethers can also be made by this method:—

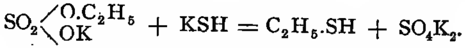


$$C_2H_5.SK + C_3H_7\ Cl = \begin{matrix}C_2H_5\\C_3H_7\end{matrix}\!\!>\!S + KCl.$$

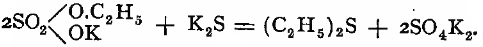
Further, they are produced when the mercury mercaptides are subjected to heat:—

$$(C_2H_5.S)_2Hg = (C_2H_5)_2S + HgS.$$

(2) By distilling salts of the sulphuric esters with potassium sulphydrate or potassium sulphide (see p. 119):—



$$SO_2\!<\!\begin{matrix}O.C_2H_5\\OK\end{matrix} + KSH = C_2H_5.SH + SO_4K_2.$$



$$2SO_2\!<\!\begin{matrix}O.C_2H_5\\OK\end{matrix} + K_2S = (C_2H_5)_2S + 2SO_4K_2.$$

The neutral esters of sulphuric acid, *e. g.*, $SO_2(O.C_2H_5)_2$ (p. 148), also yield mercaptans when heated with KSH.

(3) A direct replacement of the O of alcohols and ethers by S may be attained by phosphorus sulphide:—

$$5C_2H_5.OH + P_2S_5 = 5C_2H_5.SH + P_2O_5 \text{ and}$$
$$5(C_2H_5)_2O + P_2S_5 = 5(C_2H_5)_2S + P_2O_5.$$

The P_2O_5 is likely to react further upon the alcohols, and then phosphoric acid esters will appear simultaneously with the preceding compounds.

The *alkyl disulphides* (p. 140) are prepared just the same as the monosulphides; by distillation of salts of ethyl sulphuric acid with potassium disulphide; also, by the action of iodine upon the mercaptides:—

$$2C_2H_5.SK + I_2 = (C_2H_5)_2S_2 + 2KI.$$

A simpler method is the action of sulphuryl chloride upon the mercaptans (*Berichte*, 18, 3178):—

$$2C_2H_5.SH + SO_2Cl_2 = (C_2H_5)_2S_2 + SO_2 + 2HCl.$$

Mixed alkyl disulphides result from the action of bromine upon a mixture of two mercaptans (*Berichte*, 19, 3132).

Nascent hydrogen converts the alkyl disulphides into mercaptans, and zinc dust reduces them to mercaptides: $(C_2H_5)_2S_2 + Zn = (C_2H_5.S)_2Zn$. On heating with potassium sulphide they yield potassium mercaptides (*Berichte*, 19, 3129). See also phenyl disulphide.

The mercaptans and thio-ethers are colorless liquids, mostly insoluble in water, and possessed of a disagreeable, garlic-like odor. The metallic derivatives of the mercaptans—termed *mercaptides*—may be obtained by the double decomposition of the alkali compounds, and also by the direct action of the metallic oxides.

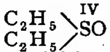
They absorb oxygen from the air and yield alkyl disulphides. They become *mercaptals* and *mercaptols* by their union with aldehydes and ketones. When oxidized with nitric acid the mercaptans unite with three atoms of oxygen, and yield the so-called sulphonic acids (p. 152):—

$$C_2H_5.SH + 3O = C_2H_5.SO_3H.$$

Ethyl Sulphonic Acid.

Conversely, the mercaptans result by the reduction of the sulphonic acids (their chlorides) (p. 152).

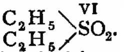
The sulphur ethers (the alkyl sulphides) also, take up one and two oxygen atoms when treated with HNO$_3$, and yield *sulphoxides* and *sulphones*:—



$$\left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\rangle \overset{\text{IV}}{SO}$$

Diethyl Sulph-oxide.

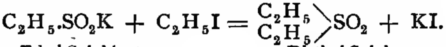
and



$$\left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\rangle \overset{\text{VI}}{SO_2}.$$

Diethyl-sulphone.

These compounds may be compared to the ketones. Nascent hydrogen (Zn and H$_2$SO$_4$) deoxidizes the sulphoxides to sulphides. The sulphones may be considered the esters of the alkyl sulphinic acids, inasmuch as they can be formed from the salts of the latter through the agency of the alkyl iodides (p. 154):—



$$C_2H_5.SO_2K + C_2H_5I = \left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\rangle SO_2 + KI.$$

Pot. Ethyl Sulphinate. Diethyl Sulphone.

Methyl Mercaptan, CH$_3$.SH, is a light liquid, that will swim on water, and boils at 20°. **Perchlor-methyl Mercaptan**, CSCl$_4$ = CCl$_3$.SCl, results from the action of chlorine upon S$_2$C (*Berichte*, 20, 2377). It is a yellow liquid, boiling at 147°. Nitric acid oxidizes it to CCl$_3$.SO$_2$Cl (p. 153). Stannous chloride converts it into thiophosgene, CSCl$_2$. **Methyl Sulphide**, (CH$_3$)$_2$S, boils at 37.5°, and combines with bromine to yield a crystalline compound, (CH$_3$)$_2$SBr$_2$. Concentrated nitric acid oxidizes methyl sulphide to sulphoxide, (CH$_3$)$_2$SO, which forms the salt (CH$_3$)$_2$SO.NO$_3$H with an excess of acid. Barium carbonate separates the free sulphoxide from this. Silver oxide produces the same compound when it acts upon the bromide, (CH$_3$)$_2$SBr$_2$. The sulphoxide is an oil, soluble in water and congealed by cold. On heating methyl sulphide with fuming nitric acid we obtain dimethyl-sulphone, (CH$_3$)$_2$SO$_2$. This is a crystalline body, fusing at 109° and boiling at 238°. **Methyl Disulphide**, (CH$_3$)$_2$S$_2$, boils at 112° C.

Ethyl Mercaptan, C$_2$H$_5$.SH, is a colorless liquid, boiling at 36°, and solidifying to a crystalline mass upon rapid evaporation. Its sp. gr. at 20° is 0.839. It is but slightly soluble in water; readily in alcohol and ether.

It may be prepared by saturating a concentrated KOH solution with hydrogen sulphide, adding potassium ethyl sulphate to this, and then distilling, when the light mercaptan will swim upon the aqueous distillate. To obtain it perfectly pure, shake with HgO, recrystallize the solid mercaptide from alcohol, and then decompose it with H_2S.

Mercury mercaptide, $(C_2H_5.S)_2Hg$, crystallizes from alcohol in brilliant leaflets, fusing at 86°, and is only slightly soluble in water. When mercaptan is mixed with an alcoholic solution of $HgCl_2$ the compound $C_2H_5.S.HgCl$ is precipitated. The potassium and sodium compounds are best obtained by dissolving the metals in mercaptan diluted with ether; they crystallize in white needles.

Ethyl Sulphide, $(C_2H_5)_2S$, obtained by the distillation of ethyl chloride with an alcoholic solution of K_2S, boils at 91°. It combines with some metallic chlorides to yield double compounds, like $(C_2H_5)_2S.HgCl_2$ and $[(C_2H_5)_2S]_2.PtCl_4$.

If oxidized with dilute nitric acid it forms the sulphoxide, $(C_2H_5)_2SO$, an oily liquid, which decomposes when distilled. Fuming nitric acid produces diethyl sulphone, $(C_2H_5)_2SO_2$, soluble in water and alcohol, and crystallizing in large, colorless plates. It melts at 70°, and boils, undecomposed, at 248°. Nascent hydrogen (zinc and sulphuric acid) converts the sulphoxide into ethyl sulphide.

Ethyl Disulphide, $(C_2H_5)_2S_2$, is obtained from ethyl mercaptan either by means of iodine or sulphuryl chloride (p. 142). It is an oil with a garlicky odor. It boils at 151°.

Propyl Mercaptan, $C_3H_7.SH$, boils at 68°, and the iso-derivative at 58-60°. *Dipropyl sulphide*, $(C_3H_7)_2S$, boils at 130-135°.

Normal Butyl Mercaptan, $C_4H_9.SH$, boils at 98°; *dibutyl sulphide* at 182°; *di-isobutyl sulphide* at 173°. The latter yields only one monoxide with nitric acid, while a dioxide is also obtained from dibutyl sulphide (*Annalen*, 175, 349).

Cetyl Sulphide, $(C_{16}H_{33})_2S$, crystallizes in shining leaflets, fusing at 57°.

Vinyl Sulphide, $(C_2H_3)_2S$ (compare p. 97), is the principal ingredient of the oil of *Allium ursinum*, and is perfectly similar to allyl sulphide. It boils at 101°; its sp. gr. is 0.9125. It forms $(C_2H_3Br_2)_2SBr_2$ with six atoms of bromine. Silver oxide changes it to vinyl oxide $(C_2H_3)_2O$ (p. 140). Like allyl sulphide, it combines with silver nitrate and mercuric chloride to form perfectly analogous compounds (*Annalen*, 241, 90).

Allyl Mercaptan, $C_3H_5.SH$, is very similar to ethyl mercaptan, and boils at 90°.

Allyl Sulphide, $(C_3H_5)_2S$, is the chief constituent of the oil of garlic (from *Allium sativum*), and is obtained by the distillation of garlic with water. It occurs in many of the *Cruciferæ*. It may be prepared artificially by digesting allyl iodide with potassium sulphide in alcoholic solution. It is a colorless, disagreeable-smelling oil, but slightly soluble in water. It boils at 140°. It forms crystalline precipitates with alcoholic solutions of $HgCl_2$ and $PtCl_4$.

With silver nitrate it yields the crystalline compound $(C_3H_5)_2S.2AgNO_3$.

Allyl mustard oil is produced on heating the mercury derivative with potassium sulphocyanide. Vinyl mustard oil is prepared in an analogous manner.

Sulphine Compounds. The sulphides of the alcohol radicals (thio-ethers) combine with the iodides (also with bromides and chlorides) of the alcohol radicals at ordinary temperatures, more rapidly on application of heat, and form crystalline compounds:—

$$(C_2H_5)_2S + C_2H_5I = \underset{\text{Triethyl Sulphine Iodide.}}{(C_2H_5)_3\overset{IV}{S}I.}$$

These are perfectly analogous to the halogen derivatives of the strong basic radicals (the alkali metals). By the action of moist silver oxide the halogen atom in them may be replaced by hydroxyl, and hydroxides similar to potassium hydroxide be formed:—

$$(C_2H_5)_3SI + AgOH = (C_2H_5)_3S.OH + AgI.$$

The sulphine haloïds are also obtained on heating the sulphur ethers with the halogen hydrides:—

$$2(C_2H_5)_2S + HI = (C_2H_5)_2SI + C_2H_5.SH.$$

The acid chlorides react similarly. Often when the alkyl iodides act on the sulphides of higher alkyls the latter are displaced (*Berichte*, 8, 325):—

$$(C_7H_7)_2S + 3CH_3I = (CH_3)_3SI + 2C_7H_7I.$$

$(C_2H_5)_2S.CH_3I$ and $\begin{matrix}CH_3\\C_2H_5\end{matrix}\!\!>\!S.C_2H_5I$ are to be isomeric, in which case a difference of the 4 valences of S would be proven.

As in similar cases, the most recent investigations have shown them to be identical (*Berichte*, 22, Ref. 648).

The sulphine hydroxides are crystalline, efflorescent, strongly basic bodies, readily soluble in water. Like the alkalies they precipitate metallic hydroxides from metallic salts, set ammonia free from ammoniacal salts, absorb CO_2 and saturate acids, with the formation of neutral salts:—

$$(C_2H_5)_3S.OH + NO_3H = (C_2H_5)_3S.NO_3 + H_2O.$$

We thus observe that relations similar to those noted with the nitrogen group prevail with sulphur (also with selenium and tellurium). Nitrogen and phosphorus combine with four hydrogen atoms (also with alcoholic radicals) to form the groups ammonium, NH_4, and phosphonium, PH_4, which yield compounds similar to those of the alkali metals. Sulphur and its analogues combine in like manner with three monovalent alkyls, and give sulphonium and sulphine derivatives. Other metalloids and the less positive metals, like lead and tin, exhibit a perfectly similar behavior. By addition of hydrogen or alkyls they acquire a strongly basic, metallic character (see the metallo-organic compounds).

Only the sulphine derivatives of methane and ethane have been carefully studied; the former are perfectly similar to the latter.

Triethyl Sulphine Iodide, $(C_2H_5)_3SI$, obtained by heating ethyl sulphide and iodide to 100°, crystallizes from water and alcohol in rhombic plates. Platinum chloride precipitates the double salt $[(C_2H_5)_3SCl]_2.PtCl_4$, from a solution of the chloride. It forms red needles.

Triethyl Sulphine Hydroxide, $(C_2H_5)_3S.OH$, forms efflorescent crystals and possesses an alkaline reaction. Its nitrate, $(C_2H_5)_3S.O.NO_2$, crystallizes in efflorescent scales. Hydrochloric acid converts the hydroxide into chloride, $(C_2H_5)_3SCl$.

SELENIUM AND TELLURIUM COMPOUNDS.

These are perfectly analogous to the sulphur compounds. The methods of formation are also similar.

Ethyl Hydroselenide, $C_2H_5.SeH$, is a colorless, unpleasant-smelling, very mobile liquid. It combines readily with mercuric oxide to form a mercaptide.

Ethyl Selenide, $(C_2H_5)_2Se$, is a heavy, yellow oil, boiling at 108°. It unites directly with the halogens, *e. g.*, $(C_2H_5)_2SeCl_2$. It dissolves in nitric acid with formation of the oxide, $(C_2H_5)_2SeO$, which yields the salt, $(C_2H_5)_2Se(NO_3)_2$.

Methyl Telluride, $(CH_3)_2Te$, is obtained by distilling barium methyl sulphate with potassium telluride. It is a heavy, yellow oil, boiling from 80–82°. Dilute nitric acid converts it into the nitrate of the oxide, $(CH_3)_2Te(NO_3)_2$. From an aqueous solution of this salt hydrochloric acid precipitates a white, crystalline chloride, $(CH_3)_2TeCl_2$; this yields the oxide, $(CH_3)_2TeO$, with silver oxide. This is a crystalline, efflorescent compound. In properties it resembles CaO and PbO. It reacts strongly alkaline, expels ammonia from ammonium salts, and forms salts by neutralizing acids.

Methyl telluride combines with methyl iodide to form **Trimethyl tellurium iodide**, $(CH_3)_3TeI$, which passes into the strongly basic **hydroxide**, $(CH_3)_3Te.OH$, by the action of moist silver oxide. It resembles potassium hydroxide.

Tri-ethyl Tellurium Chloride, $Te(C_2H_5)_3Cl$, has been obtained by the action of zinc ethide on tellurium tetrachloride. It consists of colorless leaflets, melting at 174° C. Hydriodic acid converts it into the iodide, melting at 9° (*Berichte*, 21, 2043).

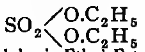
Ethyl Telluride, $(C_2H_5)_2Te$, is a reddish-colored oil, soluble in nitric acid with formation of $(C_2H_5)_2Te(NO_3)_2$. Hydrochloric acid precipitates the *chloride*, $(C_2H_5)_2TeCl_2$, from an aqueous solution of the salt. Hydriodic acid precipitates the *iodide*, $(C_2H_5)_2TeI_2$. This is an orange-red powder, fusing at 50°.

ESTERS OF THE MINERAL ACIDS.

If we compare the alcohols with the metallic bases, the esters or compound ethers (see p. 137) are perfectly analogous in constitution to the salts. We can regard them as alcohol derivatives, arising by the substitution of acid radicals for alcoholic hydrogen, or they may be viewed as derivatives of the acids formed by substituting alcohol radicals for the hydrogen of acids. The various designations of esters would indicate this:—

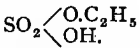
$$\underset{\text{Ethyl Nitrate.}}{C_2H_5.O.NO_2} \quad \text{or} \quad \underset{\text{Nitric Ethyl Ester.}}{NO_2.O.C_2H_5.}$$

The first view is better adapted for esters of the polyhydric alcohols, while the second answers best for those of the polybasic acids. In these all or only one hydrogen atom can be replaced by alcohol radicals; thus arise the *neutral* esters and the so-called *ether-acids*, which correspond to the acid salts:—



$$SO_2\left\langle\begin{matrix}O.C_2H_5\\O.C_2H_5\end{matrix}\right.$$

Sulphuric Ethyl Ester.

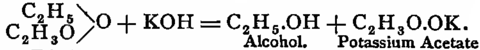


$$SO_2\left\langle\begin{matrix}O.C_2H_5\\OH.\end{matrix}\right.$$

Ethyl Sulphuric Acid.

Almost all the neutral esters are volatile; therefore the determination of their vapor density is a convenient means of establishing the molecular size and also the basicity of the acids. The ether-acids are not volatile, but soluble in water and yield salts with the bases.

All esters, and especially the ether-acids are decomposed into alcohols and acids when heated with water. Sodium and potassium hydroxides, in aqueous or alkaline solution, accomplish this with great readiness when aided by heat. The process is termed *saponification*:—



$$\left.\begin{matrix}C_2H_5\\C_2H_3O\end{matrix}\right\rangle O + KOH = \underset{\text{Alcohol.}}{C_2H_5.OH} + \underset{\text{Potassium Acetate.}}{C_2H_3O.OK.}$$

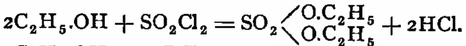
Ethyl Acetate, Ethyl Acetic Ester.

There are two synthetic methods of producing the esters that favor the views of considering them derivatives of alcohols or acids. These are:—

(1) By reacting on the acids (their silver or alkali salts) with alkylogens:—

$$NO_2.O.Ag + C_2H_5I = NO_2.O.C_2H_5 + AgI.$$

(2) By acting upon the alcohols or metallic alcoholates with acid chlorides:—



$$2C_2H_5.OH + SO_2Cl_2 = SO_2\left\langle\begin{matrix}O.C_2H_5\\O.C_2H_5\end{matrix}\right. + 2HCl.$$

$$3C_2H_5.OH + BCl_3 = B(O.C_2H_5)_3 + 3HCl.$$

In addition to these reactions, which generally occur with ease, the esters can also be prepared by allowing alcohols and acids to act directly; water is also produced:—

$$C_2H_5.OH + NO_2.OH = C_2H_5.O.NO_2 + H_2O.$$

This transposition, however, only takes place gradually, progressing with time; it is accelerated by heat, but is never complete. We always find alcohols and acids together with the esters, and they do not react any further upon each other. If the *ester* be removed, *e. g.*, by distillation, from the mixture, as it is formed, an almost perfect reaction may be attained. These relations are perfectly similar to those observed in the action of two salts (compare Inorganic Chemistry). A more comprehensive statement of the processes taking place in the action of acids and alcohols will be given under the esters of the fatty acids.

When acted upon by alcohols, the polybasic acids mostly yield the primary esters or ether-acids. The haloid acids behave just like the mono-basic acids; the alkylogens formed (see p. 93) may be termed *haloid esters* of the alcohols.

NITRIC ACID ETHERS (ESTERS).

Methyl Nitrate, $CH_3.O.NO_2$, *Nitric Methyl Ester,* is produced by distilling methyl alcohol with nitric acid. It is a colorless liquid, slightly soluble in water, and boiling at 66°. Its specific gravity, at 20°, is 1.182. When struck or heated to 150° it explodes very violently.

It is prepared by distilling a mixture of methyl alcohol (5 pts.) with sulphuric acid (10 pts.) and nitre (2 pts.), or a mixture of wood spirit and nitric acid, adding a little urea at the same time (compare ethyl nitrate).

Ethyl Nitrate. $C_2H_5.O.NO_2$, *Nitric Ethyl Ester.* When alcohol is heated with nitric acid, there is a partial oxidation of the alcohol, which causes the formation of nitrous acid and nitrous ethyl ester. If, however, we destroy the nitrous acid (best by addition of urea), pure nitric ethyl ester results.

Distil 120–150 grms. of a mixture consisting of 1 volume nitric acid (of specific gravity 1.4) and 2 volumes alcohol (80–90 per cent.), to which 1–2 grams urea have been added. Explosions sometimes occur when larger quantities are employed. The distillate is shaken with water, and the heavier ester separated from the aqueous liquid.

Ethyl nitrate is a colorless, pleasant-smelling liquid, boiling at 86°, and having a specific gravity of 1.112, at 15°. It is almost insoluble in water, and burns with a white light. It will explode if suddenly exposed to high heat. Heated with ammonia it passes into ethylamine nitrate. Tin and hydrochloric acid convert it into hydroxylamine.

The *propyl ester*, $C_3H_7.O.NO_2$, (*Berichte*, 14, 421) boils at 110°, the *iso-propyl ester* at 101–102°, and the *isobutyl ester* at 123°. *Cetyl ester*, $C_{16}H_{33}.O.NO_2$, solidifies at 10°.

NITROUS ACID ETHERS (ESTERS).

These are isomeric with the nitro-paraffins (p. 107). The group NO_2 is present in both; while, however, in the nitro-compounds nitrogen is combined with carbon, in the esters the union is effected by oxygen:—

$C_2H_5.NO_2$
Nitro-ethane.

$C_2H_5.O.NO.$
Nitrous Ethyl Ester.

The nitrous esters, as might be inferred from their different structure, decompose into alcohols and nitrous acid when acted on by alkalies. Similar treatment will not decompose the nitro-compounds. Nascent hydrogen (tin and hydrochloric acid) converts the latter into amines, while the esters yield alcohols.

Nitrous acid esters are produced in the action of nitrous acid upon the alcohols. The latter are saturated with nitrous acid vapors and distilled; or a mixture of alcohol, KNO_3 and H_2SO_4 is distilled. A late procedure consists in adding the calculated quantity of alcohol to the dilute solution of sodium nitrite. To this cold mixture add hydrochloric acid, then distil (*Berichte*, 19, 915).

Methyl Nitrite, Nitrous Methyl Ester, $CH_3.O.NO$, is an agreeable-smelling gas. When exposed to great cold, it is condensed to a yellowish liquid, boiling at — 12°.

Ethyl Nitrite, Nitrous Ethyl Ester, $C_2H_5.O.NO$, is a mobile, yellowish liquid, of specific gravity 0.947, at 15°, and boils at + 16°. It is insoluble in water, and possesses an odor resembling that of apples. It is best obtained by heating a mixture of alcohol and nitric acid with copper turnings, or may be made by distilling a mixture of alcohol and fuming nitric acid, after having stood for some hours. The distillate is shaken with water (to withdraw alcohol) and a soda solution, then dehydrated and distilled (see *Annalen*, 126, 71; *Berichte*, 21, Ref. 515).

When ethyl nitrite stands with water it gradually decomposes, nitrogen oxide being eliminated; an explosion may occur under some conditions. Hydrogen sulphide changes it into alcohol and ammonia.

Tertiary Butyl Nitrite, $C(CH_3)_3.O.NO$, boils at 77°.

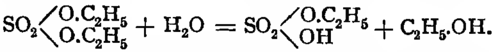
Amyl Nitrite, $C_5H_{11}.O.NO$, obtained by the distillation of fermentation amyl alcohol with nitric acid, is a yellow liquid, boiling at 96°; its sp. gr. is 0.902. An explosion takes place when the vapors are heated to 250°. Nascent hydrogen changes it into amyl alcohol and ammonia. Heated with methyl alcohol, it is transformed into methyl nitrite and amyl alcohol. The result is the same if ethyl alcohol be used (*Berichte*, 20, 656).

ESTERS OF SULPHURIC ACID (ETHYL SULPHATES).

Sulphuric acid being dibasic forms two series of esters—the neutral esters and the primary esters or ether-acids (ethereal salts) (p. 146.)

(1) The *neutral esters* are formed by the action of the alkyl iodides upon silver sulphate, SO_4Ag_2; they are also produced, in

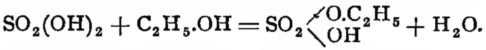
slight quantity on heating the primary esters or alcohols with sulphuric acid. They can be extracted with chloroform from the product, and are heavy liquids, soluble in ether, possess an odor like that of peppermint, and boil without decomposition. They will sink in water, and gradually decompose into a primary ester and alcohol :—



$$SO_2\begin{matrix}\diagup O.C_2H_5\\ \diagdown O.C_2H_5\end{matrix} + H_2O = SO_2\begin{matrix}\diagup O.C_2H_5\\ \diagdown OH\end{matrix} + C_2H_5.OH.$$

The *Dimethyl Ester*, $SO_2(O.CH_3)_2$—normal methyl sulphate—boils, without decomposition, at 188°. The *diethyl-ester*, $SO_2(O.C_2H_5)_2$, normal ethyl sulphate, boils at 208°, sustaining at the same time a partial decomposition. When heated with alcohol, ethyl sulphuric acid and ethyl ether are formed (*Berichte*, 13, 1699; 15, 947).

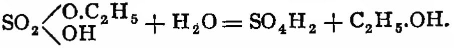
(2) The primary esters or ether-acids are produced when the alcohols are mixed with concentrated sulphuric acid :—



$$SO_2(OH)_2 + C_2H_5.OH = SO_2\begin{matrix}\diagup O.C_2H_5\\ \diagdown OH\end{matrix} + H_2O.$$

The reaction takes place only when aided by heat, and it is not complete, because the mixture always contains free sulphuric acid and alcohol (compare p. 147). To isolate the ether-acids, the product of the reaction is diluted with water and boiled up with an excess of barium carbonate. In this way the unaffected sulphuric acid is thrown out as barium sulphate; the barium salts of the ether-acids are soluble and crystallize out when the solution is evaporated. To obtain the acids in a free state their salts are treated with sulphuric acid or the lead salts (obtained by saturating the acids with lead carbonate) may be decomposed by hydrogen sulphide, and the solution allowed to evaporate over sulphuric acid.

These acids are also prepared by the union of the alkylens with concentrated sulphuric acid (p. 80). They are thick liquids, that cannot be distilled. They sometimes crystallize. In water and alcohol they dissolve readily, but are insoluble in ether. When boiled or warmed with water they break up into sulphuric acid and alcohol :—



$$SO_2\begin{matrix}\diagup O.C_2H_5\\ \diagdown OH\end{matrix} + H_2O = SO_4H_2 + C_2H_5.OH.$$

When distilled they yield sulphuric acid and alkylens (p. 80.) Upon heating them with alcohols simple and mixed ethers (p. 136) are produced.

They show a strongly acid reaction and furnish salts that dissolve quite readily in water, and crystallize without great trouble. The salts gradually change to sulphates and alcohol when they are boiled with water. Those with the alkalies are frequently applied in different reactions. Thus with KSH and K_2S they yield mercaptans and thio-ethers (p. 140); with salts of fatty acids they furnish esters, and with KCN the alkyl cyanides, etc.

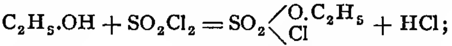
Methyl Sulphuric Acid, $SO_4(CH_3)H$, is a thick oil, that does not solidify at —30°. The potassium salt $(SO_4)CH_3K + \frac{1}{2}H_2O)$, forms deliquescent leaflets. The barium salt, $(CH_3.SO_4)_2Ba + 2H_2O$, crystallizes in plates.

Ethyl Sulphuric Acid, $SO_4(C_2H_5)H$, is obtained by mixing 1 part alcohol with 2 parts concentrated sulphuric acid, and by the union of C_2H_4 with sulphuric acid (p. 81). It is a thick, non-crystallizable liquid, having, at 16°, a specific gravity of 1.316. The potassium salt, $SO_4(C_2H_5)K$, is anhydrous; it crystallizes in plates, that dissolve quite readily. The barium and calcium salts crystallize in large tablets with two molecules of H_2O each. Consult *Annalen*, 218, 299, for two different barium salts of methyl and ethyl sulphuric acid.

Amyl Sulphuric Acid, $SO_4(C_5H_{11})H$. Two isomeric barium amyl sulphates are obtained by mixing ordinary fermentation amyl alcohol with sulphuric acid, and then neutralizing with barium carbonate. These salts both crystallize in large tablets, and show varying solubility in water, and may be separated by repeated crystallization. The more sparingly soluble salt is produced in the greater abundance and furnishes isobutyl carbinol, while active amyl alcohol is obtained from the more readily soluble salt (p. 131).

Allyl Sulphuric Acid, $SO_4(C_3H_5)H$, has been made from allyl alcohol and sulphuric acid.

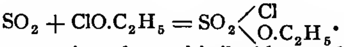
The *chlorides* or *chloranhydrides* of the ether sulphuric acids $\left(SO_2\begin{cases}O.C_2H_5\\Cl\end{cases}\right)$, called esters of chlorsulphonic acids, result in the action of sulphuryl chloride upon the alcohols:—



$$C_2H_5.OH + SO_2Cl_2 = SO_2\begin{cases}O.C_2H_5\\Cl\end{cases} + HCl;$$

Chloride of Ethyl
Sulphuric Acid.

and by the action of SO_2 upon the esters of hypochlorous acids (*Berichte*, 19, 860):—



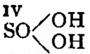
$$SO_2 + ClO.C_2H_5 = SO_2\begin{cases}Cl\\O.C_2H_5\end{cases}.$$

All are liquids with penetrating odor, and boil with scarcely any decomposition. Cold water decomposes them very slowly, without the formation of the ether acids. These they yield, together with ethyl chlorides, on adding alcohol to them. The reaction is rather energetic.

Chloride of Ethyl Sulphuric Acid, $C_2H_5.O.SO_2Cl$, boils about 152°. *Methyl Sulphuric Chloride*, $CH_3.O.SO_2Cl$, boils at 132°.

SULPHUROUS ACID ETHERS (ESTERS).

The empirical formula of sulphurous acid, SO_3H_2, may have one of two possible structures:—



$$\overset{IV}{SO}\begin{cases}OH\\OH\end{cases} \quad \text{or} \quad \overset{VI}{H}SO_2.OH.$$

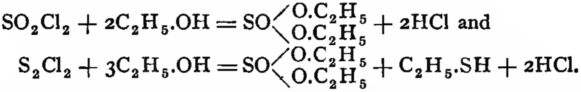
Symm. Sulphurous Acid. Unsymm. Sulphurous Acid.

The ordinary sulphites correspond to formula 2, and it appears that in them one atom of metal is in direct combination with sulphur:—

$$\underset{\text{Silver Sulphite.}}{Ag.SO_2.OAg.} \qquad \underset{\text{Prim. Pot. Sulphite.}}{K.SO_2.OH.}$$

This is evident from the following considerations:—

(1) *Esters of Symmetrical Sulphurous Acid.*
These are produced in the action of thionyl chloride, $SOCl_2$, or sulphur monochloride, S_2Cl_2, upon alcohols:—



$$SO_2Cl_2 + 2C_2H_5.OH = SO\left\langle\begin{matrix}O.C_2H_5\\O.C_2H_5\end{matrix}\right. + 2HCl \text{ and}$$
$$S_2Cl_2 + 3C_2H_5.OH = SO\left\langle\begin{matrix}O.C_2H_5\\O.C_2H_5\end{matrix}\right. + C_2H_5.SH + 2HCl.$$

The mercaptan that is simultaneously formed sustains further decomposition. The sulphites thus produced are volatile liquids, insoluble in water, with an odor resembling that of peppermint, and decomposed by water, especially when heated, into alcohols and sulphurous acid.

Sulphurous Methyl Ester, $SO(O.CH_3)_2$, methyl sulphite, boils at 121°.

The **Ethyl-Ester,** $SO(O.C_2H_5)_2$, boils at 161°. Its specific gravity at 0° is 1.106. PCl_3 converts it into the chloride, $SO\left\langle\begin{matrix}Cl\\O.C_2H_5\end{matrix}\right.$, a liquid boiling at 122°, and decomposed by H_2O into alcohol, SO_2 and HCl. It is isomeric with ethyl sulphonic chloride, $C_2H_5.SO_2Cl$ (p. 153). On mixing the ester with a dilute solution of the equivalent amount of KOH, a potassium salt, $SO.\left\langle\begin{matrix}O.C_2H_5\\OK\end{matrix}\right.$, separates in glistening scales. This is viewed as a salt of the unstable ethyl sulphurous acid.

(2) *Esters of the Unsymmetrical Sulphurous Acid.*—These are formed by the action of silver sulphite upon the alkyl iodides in ethereal solution:—

$$Ag.SO_2.OAg + 2C_2H_5I = C_2H_5.SO_2.O.C_2H_5 + 2AgI.$$

One of the alkyl groups is joined to sulphur, the other to oxygen. When heated with water the latter one only is separated as alcohol, and sulphonic acids result:—

$$C_2H_5.SO_2.O.C_2H_5 + H_2O = \underset{\text{Ethyl Sulphonic Acid.}}{C_2H_5.SO_2.OH} + C_2H_5.OH.$$

Conversely, the esters can be prepared from the sulphonic acids, by acting on their salts with alkyl iodides or upon the sodium alcoholates with the chlorides of the sulphonic acids:—

$$\underset{\text{Ethyl Sulphonic Chloride.}}{C_2H_5.SO_2Cl} + C_2H_5.ONa = \underset{\text{Ethyl Sulphonic Ethyl Ester.}}{C_2H_5.SO_2.O.C_2H_5} + NaCl.$$

Hence, the esters formed from silver sulphite may be regarded as esters of the sulpho-acids. They boil much higher than the isomeric esters of symmetrical sulphurous acid. They are distinguished from the latter by having but one of their alkyl groups separated out by alkalies (see above).

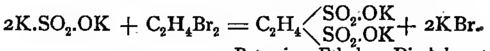
Ethyl Sulphonic Ethyl Ester, $C_2H_5.SO_2.O.C_2H_5$, produced as above described, boils at 213.4°, and has a sp. gr. of 1.171 at 0°.

The *methyl ester*, $C_2H_5.SO_2.O.CH_3$, boils at 198°.

3. *Sulpho-acids*, $C_nH_{2n+1}.SO_2.OH$.

The sulpho- or sulphonic acids, which contain the group $—SO_2OH$ attached to carbon, may be viewed as esters of unsymmetrical sulphurous acid, HSO_2OH, inasmuch as they are produced from its neutral esters by the separation of an alkyl group (p. 151). Furthermore, their salts are directly obtained from the alkaline sulphites (preferably ammonium sulphite) by heating them with alkylogens (in concentrated aqueous solution to 120–150°):—

$$K.SO_2.OK + C_2H_5I = \underset{\text{Potassium Ethyl Sulphonate.}}{C_2H_5.SO_2.OK} + KI.$$



$$2K.SO_2.OK + C_2H_4Br_2 = C_2H_4\begin{cases} SO_2.OK \\ SO_2.OK \end{cases} + 2KBr.$$

Potassium Ethylene Disulphonate.

The oxidation of mercaptans and alkyl disulphides (p. 142) (also sulphocyanides) with nitric acid also affords the sulpho-acids:—

$$\underset{\text{Ethyl Mercaptan.}}{C_2H_5.SH} + 3O = \underset{\text{Ethyl Sulphonic Acid.}}{C_2H_5.SO_2.OH.}$$

Conversely, these sulpho-acids can be again reduced to mercaptans (by action of zinc and hydrochloric acid upon their chlorides—as $C_2H_5.SO_2Cl$): $C_2H_5\ SO_2Cl + 3H_2 = C_2H_5.SH + HCl + 2H_2O$. They may also be obtained by oxidizing the sulphinic acids and can be again converted into the latter (see p. 154). All these reactions plainly indicate that in the sulpho-acids the alkyl group is joined to sulphur, and that, therefore, it is very probable that in the sulphites the one atom of metal is directly combined with sulphur. Finally, the sulpho-acids can be prepared by the action of sulphuric acid or sulphur trioxide (SO_3) upon alcohols, ethers and various other bodies. This reaction is very general and easily executed with the benzene derivatives.

These acids are thick liquids, readily soluble in water, and generally crystallizable. They suffer decomposition when exposed to heat, but are not altered when boiled with alkaline hydroxides. When fused with solid alkalies they break up into *sulphites* and alcohols:—

$$C_2H_5.SO_2.OK + KOH = KSO_2.OK + C_2H_5.OH.$$

PCl_5 changes them to chlorides, *e.g.*, $C_2H_5.SO_2Cl$, which become mercaptans through the agency of hydrogen, or by the action of sodium alcoholates pass into the neutral esters—$C_2H_5.SO_3.C_2H_5$ (p. 151).

Methyl Sulphonic Acid, $CH_3.SO_3H$, is a thick, uncrystallizable liquid, soluble in water. When heated above 130° it sustains decomposition. In order to obtain the pure acid it is converted into the lead salt, the solution of which is treated with H_2S, the lead sulphide filtered off and the filtrate concentrated.

Its salts are readily soluble in water and crystallize well. The barium salt, $(CH_3.SO_3)_2Ba + 1\frac{1}{2}H_2O$, crystallizes in rhombic plates. Methyl sulphonic chloride, $CH_3.SO_2Cl$, boils near 160° and is slowly decomposed by water into the acid and hydrogen chloride.

The following is an interesting method of preparing methyl sulphonic acid: Moist chlorine is allowed to act upon carbon disulphide, CS_2, when there is produced the compound, $CCl_4.SO_2$, which must be considered as the chloride of trichlormethyl sulphonic acid, $CCl_3.SO_2Cl$. It is colorless and crystalline; it fuses at 135°, and boils at 170°. It is soluble in alcohol and ether, but not in water. Its odor resembles that of camphor, and excites tears. To prepare the chloride a mixture of 500 gr. HCl, 300 grms. coarse-grained $Cr_2O_7K_2$, 200 gr. nitric acid and 30 gr. CS_2, are allowed to stand in an open flask. Water is then added, to dissolve the salts, and the crystals of $CCl_4.SO_2$ are filtered off.

On boiling the chloride with potassium or barium hydrate salts of trichlormethyl sulphonic acid, $CCl_3.SO_3H$, are formed. The barium salt, $(CCl_3.SO_3)_2Ba + H_2O$, crystallizes in leaflets. Sulphuric acid releases the acid from it. It consists of deliquescent prisms. Nascent hydrogen (sodium amalgam) in an aqueous solution of the acid produces successively $CHCl_2.SO_3H$, $CH_2Cl.SO_3H$, and, finally, $CH_3.SO_3H$—methyl sulphonic acid. These reactions represent one of the first instances of the conversion of an inorganic (mineral) substance (CS_2) into a so-called organic derivative.

Ethyl Sulphonic Acid, $C_2H_5.SO_3H$, is a thick, crystallizable liquid.

Its lead salt, $(C_2H_5.SO_3)_2Pb$, crystallizes in readily soluble leaflets. Concentrated nitric acid oxidizes it to ethyl sulphuric acid, $SO_4(C_2H_5)H$. Its *chloride*, $C_2H_5.SO_2Cl$, is a liquid, boiling at 173°. Its *ethyl ester*, $C_2H_5.SO_3.C_2H_5$, boils at 213.4° (p. 151).

ESTERS OF THIO-SULPHURIC ACID (AND ALKYL THIO-SULPHONIC ACIDS).

On p. 151 we saw how the alkyl sulphonic acids were obtained from the sulphites by the alkyl iodides. In the same way the corresponding *alkyl thiosulphonic acids* can be prepared from the salts of thiosulphuric acid (hyposulphurous acid):—

$$KS.SO_3K + C_2H_5I = C_2H_5.S.SO_3K + KI.$$

Only the primary saturated alkyl iodides, however, react in this way (*Berichte*, 15, 1939). The ethyl compound can be made, too, by letting iodine act on a mixture of mercaptan and sodium sulphite, Na_2SO_3.

The salts of these acids crystallize well. When boiled with hydrochloric acid they are decomposed into mercaptans and primary sulphates. When heated they break up into alkyl disulphides, $(C_2H_5)_2S_2$, and dithionates $(SO_4K_2 + SO_2)$.

The **Alkyl Thiosulphonic Acids**, $R.SO_2.SH$, differ from the alkyl thiosulphuric acids. They are formed by the action of the chlorides of sulpho-acids upon potassium sulphide: $C_2H_5.SO_2Cl + K_2S = KCl + C_2H_5.SO_2.SK$. The esters, $R.SO_2SK$, of this new class were formerly called alkyl disulphoxides, $R_2S_2O_2$, and are obtained from the alkali salts by the action of the alkyl bromides (*Berichte*, 15, 123), $C_2H_5.SO_2.SK + C_2H_5Br = C_2H_5.SO_2.SK + KBr$; and by the oxidation of mercaptans and alkyl disulphides with dilute nitric acid: $(C_2H_5)_2S_2 + O_2 = C_2H_5.SO_2.SC_2H_5$. These esters are liquids, insoluble in water, and possessed of a disgusting onion-like odor. When distilled they suffer partial decomposition, but in a current of steam volatilize undecomposed. They are saponified by the alkalies, forming sulphinic acids and disulphides, while the latter, in part, decompose into sulphinic acids and mercaptans (*Berichte*, 19, 1241). With potassium sulphide the esters yield alkyl thiosulphonates and mercaptides (*Berichte*, 19, 3131). Zinc and sulphuric acid reduce the esters to disulphides and mercaptans, while zinc dust changes them to alkyl sulphinic acids (zinc salts) and zinc mercaptides. Nitric acid oxidizes the esters to two molecules of the sulphinic acids. **Ethyl Thiosulphuric Ethyl Ester**, $C_2H_5.SO_2.S.C_2H_5$, boils from 130°–140°.

Esters of Hydrosulphurous Acid—Sulphinic Acids. Two structural formulas are possible for hydrosulphurous acid: $H.\overset{IV}{S}O.OH$ and $\begin{matrix}H\\H\end{matrix}\!\!>\overset{VI}{S}O_2$. Replace one hydrogen atom and the sulphinic acids result, *e.g.*: (1) $C_2H_5.\overset{IV}{S}O.OH$ or (2) $\begin{matrix}C_2H_5\\H\end{matrix}\!\!>\overset{VI}{S}O_2$. Both forms are probably identical or tautomeric (p. 54), whereas their alkyl derivatives are isomeric:—

$C_2H_5.SO.O.C_2H_5$	and	$\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\!\!>SO_2$.
Ethyl Sulphinic Ester.		Diethyl-sulphone.

These relations are exactly analogous to those of the isomeric esters of sulphurous acid (p. 151).

When SO_2 acts upon the zinc alkyls, the sulphinic acids (their zinc salts) result:—

$(C_2H_5)_2Zn + 2SO_2 = (C_2H_5.SO_2)_2Zn$, just as the carbonic acids (*e. g.*, $C_2H_5.CO_2H$) are produced by the action of CO_2.

A simpler method would be to let zinc dust act upon the chlorides of the sulphonic acids: $2C_2H_5.SO_2Cl + 2Zn = (C_2H_5.SO_2)_2Zn + ZnCl_2$. To obtain the free acids the zinc salts are converted into barium salts and these, in turn, decomposed by sulphuric acid. The sulphinic acids are thick, strongly acid liquids, decomposed by heat. Their sodium salts are formed in the oxidation of the oxysodium mercaptides in the air: $C_2H_5.SNa + O_2 = C_2H_5.SO_2Na$.

The sulphones (p. 142) are produced in the action of alkyl iodides upon the alkaline sulphonates, while the *real esters* result from the etherification of the acids with alcohol and hydrochloric acid, or by the action of chlorcarbonic esters upon the sulphinates (*Berichte*, 18, 2493): $R.SO_2Na + Cl.CO_2R = R.SO.OR + CO_2 + NaCl$. When these esters are saponified by alcohol or water they break up into alcohol and sulphinic acid, while the isomeric sulphines are not altered. Free sulphinic acids are not very stable; they rapidly oxidize to sulphonic acids. Potassium permanganate and acetic acid convert the sulphinic esters into sulphonic esters (*Berichte*, 19, 1225), whereas the isomeric sulphones remain unchanged. **Methyl Sulphinic Acid**, $CH_3.SO_2H$, and **Ethyl Sulphinic Acid**, $C_2H_5.SO_2H$, are liquids, dissolving readily in water. In aqueous solution they soon decompose with the separation of sulphur.

ESTERS OF CHLORIC ACIDS.

Ethyl Perchlorate, $ClO_3.O.C_2H_5$, is obtained by the action of ethyl iodide upon silver perchlorate. It is a colorless liquid that explodes when heated.

The **Esters** of hypochlorous acid, ClOH, form on mixing concentrated aqueous solutions of hypochlorous acid with alcohol. They separate as yellow oils. When carefully heated they boil without decomposition, but if overheated they explode with great violence (*Berichte*, 18, 1767, and 19, 857).

Methyl Hypochlorite, $ClOCH_3$, boils at 12°; **Ethyl Hypochlorite**, $ClOC_2H_5$, boils at 36°. Both have a penetrating odor that attacks the respiratory organs powerfully.

Sulphur dioxide converts these esters into chlorsulphonic esters (p. 150), while with KCN they yield chlorimide carbonic acid esters, $C(NCl)\ (O.C_2H_5)_2$ (see these).

ESTERS OF BORIC ACID.

The esters of the tribasic acid, $B(OH)_3$, are formed along with those of the monobasic acid, BO.OH, when BCl_3 acts upon the alcohols. The first are volatile; thick liquids, while the second decompose when distilled. Acid esters are not known. Water decomposes both the preceding varieties.

Methyl Borate, $B(O.CH_3)_3$, boils at 65°.

Ethyl Borate, $B(O.C_2H_5)_3$, is obtained by distilling potassium ethyl sulphate together with borax. It boils at 119°.

ESTERS OF THE PHOSPHORIC ACIDS.

Tribasic phosphoric acid, $PO(OH)_3$, yields three series of esters—the primary, secondary and tertiary, all of which are thick liquids. Only the last volatilize without decomposition.

Triethyl Phosphoric Ester, $PO.(O.C_2H_5)_3$, is formed when phosphorus oxychloride acts upon sodium ethylate:—

$$POCl_3 + 3C_2H_5.ONa = PO(O.C_2H_5)_3 + 3NaCl.$$

A thick liquid, soluble in water, alcohol and ether, and boiling at 215°. The aqueous solution decomposes readily into diethyl-phosphoric acid, the lead salt of which is made by boiling with PbO.

Diethyl Phosphoric Acid, $PO\left\{\begin{array}{l}(CO.C_2H_5)_2,\\ OH\end{array}\right.$ is obtained by decomposing the lead salt with H_2S. It is a thick syrup. The lead salt crystallizes in silky needles. When heated it passes into the triethyl ester and lead monoethyl phosphate, insoluble in water. The acid of this last salt has the formula $PO(OH)_2.O.C_2H_5$.

The esters of symmetrical phosphorous acid, $P(OH)_3$, result when PCl_3 acts on the alcohols. Triethyl phosphite, $P(O.C_2H_5)_3$, boils at 191°.

Acids of the structure $C_2H_5.PO(OH)_2$, corresponding to the sulpho-acids, $C_2H_5.SO_2.OH$, (p. 152) may be derived from the unsymmetrical phosphorous acid, $HPO(OH)_2$. They are produced by the oxidation of primary phosphines (see these) with nitric acid:—

$$P(CH_3)H_2 + O_3 = CH_3.PO(OH)_2.$$

They are spermaceti-like, crystalline bodies, soluble in water and reacting strongly acid. They furnish both acid and neutral salts, that are mostly crystallizable.

Methyl Phosphite, $CH_3PO(OH)_2$, melts at 105°. PCl_5 converts it into $CH_3.POCl_2$, which fuses at 32°, and boils at 163°. Water again produces the acid from the chloride.

Ethyl Phosphite, $C_2H_5.PO(OH)_2$, melts at 44°.

PCl_3 converts aldehydes into compounds, which yield oxy-alkyl phosphorous acids, *e. g.*, $CH_3.CH.OH.PO(OH)_2$ (*Berichte*, 18, Ref. 111), when treated with water.

From hypophosphorous acid, $H_2.PO.OH$, we obtain similar compounds that can be called *phosphinic acids*. They result when nitric acid acts on the secondary phosphines:—

$$P(CH_3)_2H + O_2 = (CH_3)_2PO.OH,$$

Dimethyl Phosphinic Acid, $(CH_3)_2PO.OH$, resembles paraffin, fuses at 76° and volatilizes without decomposition.

ESTERS OF ARSENIC ACIDS.

Ethyl Arsenate, $AsO(O.C_2H_5)_3$, is the product of the action of ethyl iodide upon silver arsenate, AsO_4Ag_3. It is a liquid, boiling at 235°.

The esters of arsenious acid, $As(OH)_3$, form when $AsBr_3$ is distilled with sodium alcoholates. They distil without decomposition. Water immediately changes them to arsenious acid and alcohols. The methyl ester, $As(O.CH_3)_3$, boils at 128°; the ethyl ester at 166°.

Arsenic compounds analogous to the phosphorous and phosphinic acids, $C_2H_5.PO(OH)_2$ and $(C_2H_5)_2PO.OH$, exist. They are: methyl arsinic acid, $CH_3.AsO(OH)_2$, and dimethyl arsinic acid, $(CH_3)_2AsO.OH$, or **cacodylic acid.** These will be considered with arsenic alcoholic radicals.

ESTERS OF SILICIC ACIDS.

These are obtained by the action of $SiCl_4$ and $SiFl_4$ upon alcohols or sodium alcoholates. The esters of normal silicic acid, $Si(OH)_4$, of metasilicic acid, $SiO(OH)_2$, and disilicic acid, $Si_2O_7H_2$, are formed together and can be separated by fractional distillation.

The normal *Methyl Ester*, $Si(O.CH_3)_4$, boils at 120–122°; *methyl disilicate*, $Si_2O_7(CH_3)_6$, at 202°.

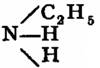
The *Ethyl Ester*, $Si(O.C_2H_5)_4$, boils at 165°. *Ethyl disilicate*, $Si_2O_7(C_2H_5)_6$, which can also be produced by action of silicon oxychloride, Si_2OCl_6, on alcohol, boils at 236°; ethyl-metasilicate, $SiO.(O.C_2H_5)_2$, boils at 360°.

These derivatives on standing awhile in moist air, or by addition of water, slowly decompose with separation of silicic acid, which sometimes solidifies to a transparent hard glass.

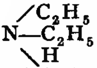
AMINES.

Among the derivatives of carbon exists a series of very basic bodies, which have been designated organic bases or alkaloids. They all contain nitrogen and are viewed as ammonia derivatives; this accounts for their basic character. We will consider here only the *monamines* derived from ammonia by the replacement of hydrogen by monovalent alkyls.

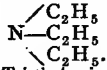
One, two and three hydrogen atoms of the ammonia molecule may suffer this replacement, thus yielding the *primary*, *secondary* and *tertiary amines* (also called amide, imide, and nitrile bases):—



Ethylamine.



Diethylamine.



Triethylamine.

Derivatives also exist that correspond to the ammonium salts and hypothetical ammonium hydroxide, $NH_4.OH$:—

$(C_3H_5)_4\overset{v}{N}Cl$
Tetra-ethyl Ammonium Chloride.

$(C_2H_5)_4\overset{v}{N}.OH.$
Tetra-ethyl Ammonium Hydroxide.

The following methods are the most important for preparing the above compounds:—

(1) The iodides or bromides of the alcohol radicals are heated to 100°, in sealed tubes, with alcoholic ammonia (*A. W. Hofmann*, 1849). In this way the alkyl displaces the hydrogen of ammonia; the hydrogen haloid formed at the same time combines with the amine and yields ammonium salts:—

$$\begin{aligned} NH_3 + C_2H_5I &= NH_2(C_2H_5).HI \\ NH_3 + 2C_2H_5I &= NH(C_2H_5)_2.HI + HI \\ NH_3 + 3C_2H_5I &= N(C_2H_5)_3.HI \quad + 2HI. \end{aligned}$$

When these salts are distilled with sodium or potassium hydroxide, free amines pass over:—

$$NH(C_2H_5)_2.HI + KOH = NH(C_2H_5)_2 + KI + H_2O.$$

It is interesting to know that the primary alkyl iodides form both secondary and tertiary amines, while the secondary alkyl iodides (like isopropyl iodide) only furnish primary amines (also alkylens) (*Berichte*, 15, 1288).

In the same process tertiary amines further unite with alkyl iodides and form tetra-alkyl ammonium salts:—

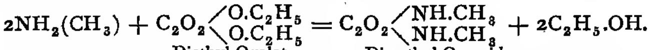
$$N(C_2H_5)_3 + C_2H_5I = \overset{v}{N}(C_2H_5)_4I.$$

These are *not* decomposed when distilled with KOH; but if treated with moist silver oxide they yield *ammonium hydroxides* :—

$$N(C_2H_5)_4I + AgOH = N(C_3H_5)_4.OH + AgI.$$

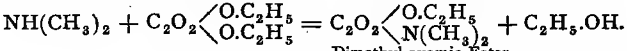
By the action of primary alkylogens upon ammonia, a mixture of primary, secondary and tertiary amine salts and those of the ammonium bases, always results. The latter may be easily obtained pure by distilling the mixture with KOH, when the amines pass over and the ammonium bases make up the residue, inasmuch as their halogen compounds are not decomposed by alkalies.

Fractional distillation is a poor means of separating the amines. The following procedure serves this purpose better (*Berichte*, 8, 760): The mixture of the dry bases is treated with diethyl oxalate, when the primary amine, *e. g.*, methylamine, is changed to diethyl oxamide, which is soluble in water; dimethylamine is converted into the ester of dimethyl oxamic acid (see oxalic acid compounds); and trimethylamine is not acted upon :—



$$2NH_2(CH_3) + C_2O_2\Big\langle\begin{matrix}O.C_2H_5\\O.C_2H_5\end{matrix} = C_2O_2\Big\langle\begin{matrix}NH.CH_3\\NH.CH_3\end{matrix} + 2C_2H_5.OH.$$

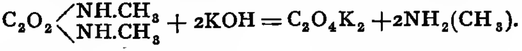
Diethyl Oxalate. Dimethyl Oxamide.



$$NH(CH_3)_2 + C_2O_2\Big\langle\begin{matrix}O.C_2H_5\\O.C_2H_5\end{matrix} = C_2O_2\Big\langle\begin{matrix}O.C_2H_5\\N(CH_3)_2\end{matrix} + C_2H_5.OH.$$

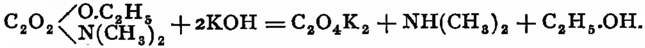
Dimethyl-oxamic Ester.

When the reaction-product is distilled the unaltered trimethylamine passes over. Water will extract the dimethyl oxamide from the residue; on distillation with caustic potash it becomes *methylamine* and potassium oxalate :—



$$C_2O_2\Big\langle\begin{matrix}NH.CH_3\\NH.CH_3\end{matrix} + 2KOH = C_2O_4K_2 + 2NH_2(CH_3).$$

The insoluble dimethyl-oxamic ester is converted, by distillation with potash, into *dimethylamine* :—



$$C_2O_2\Big\langle\begin{matrix}O.C_2H_5\\N(CH_3)_2\end{matrix} + 2KOH = C_2O_4K_2 + NH(CH_3)_2 + C_2H_5.OH.$$

Another procedure furnishing a partial separation of the amines depends on their varying behavior towards carbon disulphide. The free bases (in aqueous, alcoholic or ethereal solution) are digested with CS_2, when the primary and secondary amines form salts of the alkyl dithio-carbaminic acids (see these), while the tertiary amines remain unaffected, and may be distilled off. On boiling the residue with $HgCl_2$ or $FeCl_3$, a part of the primary amine is expelled from the compound as mustard oil (*Berichte*, 14, 2754 and 15, 1290).

The esters of nitric acid, when heated to 100° with alcoholic ammonia, react in a manner analogous to the alkyl iodides :—

$$C_2H_5.O.NO_2 + NH_3 = C_2H_5.NH_2 + HNO_3.$$

This reaction is often very convenient for the preparation of the primary amines (*Berichte*, 14, 421).

Mono-, di-, and tri-alkylamines are obtained by directly heating the alcohols to 250–300° with zinc-ammonium chloride (*Berichte*, 17, 640).

(2) The ethers of isocyanic or isocyanuric acid are distilled with potassium hydroxide (*Würtz*, 1848):—

$$CO:N.CH_3 + 2KOH = NH_2.CH_3 + CO_3K_2.$$

Cyanic acid is changed to ammonia in precisely the same manner:—

$$CO:NH + 2KOH = NH_3 + CO_3K_2.$$

In the above reaction only primary amines are produced.

To convert alcoholic radicals into corresponding amines, the iodides are heated together with silver cyanate; the product of the reaction is then mixed with pulverized caustic soda, and distilled in an oil bath (*Berichte*, 10, 131).

Above we observed the decomposition of the isocyanic ethers by alkalies. Their analogues in constitution—the isothio-cyanic ethers (the mustard oils, etc.,)—are also broken up into primary amines by sulphuric acid.

3. Warm the isocyanides of the alkyls with dilute hydrochloric acid; formic acid will split off (*A. W. Hofmann*):—

$$C_2H_5.NC + 2H_2O = C_2H_5.NH_2 + CH_2O_2.$$

The isocyanides are obtained by heating the alkyl iodides with silver cyanide (see these).

(4) By the action of nascent hydrogen upon the nitriles or alkyl cyanides (Mendius):—

$$\underset{\text{Hydrogen Cyanide.}}{HCN} + 2H_2 = \underset{\text{Methylamine.}}{CH_3.NH_2}.$$

$$\underset{\text{Acetonitrile.}}{CH_3.CN} + 2H_2 = \underset{\text{Ethylamine.}}{CH_3.CH_2.NH_2}.$$

A more advantageous course consists in allowing metallic sodium to act upon the nitrile dissolved in absolute alcohol. In this way the dicyanides can be converted into diamines (*Berichte*, 18, 2957; 19, 783; 22, 812).

(5) By action of nascent hydrogen (HCl and Zn) upon the nitro-paraffins (p. 106):—

$$CH_3.NO_2 + 3H_2 = CH_3.NH_2 + 2H_2O.$$

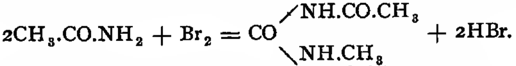
(6) A method entirely new, and especially adapted to the formation of primary amines, consists in the transformation of fatty acids (*A. W. Hofmann*, *Berichte*, 15, 762). The amides of these acids are converted, through the agency of Br and KOH, into bromamides:—

$$C_2H_5.CO.NH_2 + Br_2 + KOH = C_2H_5.CO.NHBr + KBr + H_2O.$$

On further heating with alkali, carbon dioxide escapes and primary amines result:—

$$C_2H_5.CO.NHBr + 3KOH = C_2H_5.NH_2 + CO_3K_2 + KBr + H_2O.$$

When 1 molecule bromine and 2 molecules of the amide react, the product consists of mixed ureas:—



$$2CH_3.CO.NH_2 + Br_2 = CO\begin{cases} NH.CO.CH_3 \\ NH.CH_3 \end{cases} + 2HBr.$$

Methyl Aceto-urea.

The fatty-acid amides, with more than 5 C-atoms, not only yield amines, but also large quantities of the nitriles of the next lower acids:—

$C_8H_{17}.CO.NH_2$ yields $C_7H_{15}.CN.$

In this way CO is eliminated, and amines form. These yield dibromides with bromine, and by the further action of KOH are changed to nitriles (*Berichte*, 17, 1406, 1920):—

$C_8H_{17}.NBr_2(C_7H_{15}.CH_2NBr_2)$ yields $C_7H_{15}.CN.$

These reactions are also adapted to the conversion of acid amides of the benzene series into amines (*Berichte*, 18, 2734, and 19, 1822).

(7) For the conversion of the aldehydes and ketones into their corresponding primary amines, their phenylhydrazine derivatives are treated with nascent hydrogen; best by the action of sodium amalgam and glacial acetic acid upon the alcoholic solutions (*Berichte*, 19, 1925; 22, 1854):—

$$CH_3.CH{:}N_2H.C_6H_5 + 2H_2 = CH_3.CH_2.NH_2 + C_6H_5.NH_2.$$

The primary amines can also be obtained, in a similar manner, from the hydroxylamine derivatives of the aldehydes and ketones (see the aldoximes and acetoximes) (*Berichte*, 19, 3232).

The methods above are those ordinarily employed; others exist for the production of amines; *e. g.*, they arise in the decomposition of complex nitrogenous derivatives, as shown in the case of the amido-acids.

Tertiary, secondary and primary amines may also be obtained by the dry distillation of the halogen salts of the ammonium bases:—

$$\begin{aligned} N(CH_3)_4Cl &= N(CH_3)_3 + CH_3Cl \\ N(CH_3)_3HCl &= NH(CH_3)_2 + CH_3Cl \\ NH(CH_3)_2HCl &= NH_2(CH_3) + CH_3Cl, \text{ etc.} \end{aligned}$$

These reactions serve for the commercial production of methyl chloride from trimethylamine.

On a large scale, the amines are best prepared by acting on the alkyl bromides with ammonia (*Berichte*, 22, 700).

The amines are very similar to ammonia in their deportment. The lower members are gases, with ammoniacal odor, and are very readily soluble in water; their combustibility distinguishes them from ammonia. The higher members are liquids, soluble in water, and only the highest are sparingly soluble. The amines are best dehydrated by distillation over barium oxide. Their basicity is greater than that of ammonia, and increases with the number of alkyls introduced; the tertiary amines are stronger bases than the secondary, and the latter stronger than the primary. Therefore, they can expel ammonia from the ammonium salts. Like ammonia, they unite directly with acids to form salts, which differ from ammoniacal salts by their solubility in alcohol. They combine with some metallic chlorides, and afford compounds perfectly analogous to the ammonium double salts; *e. g.*:—

$$[N(CH_3)H_3Cl]_2PtCl_4. \quad N(CH_3)H_3Cl.AuCl_3. \quad [N(CH_3)_3HCl]_2HgCl_2.$$

The ammonia in the alums, the cuprammonium salts and other compounds may be replaced by amines.

The behavior of amines with nitrous acid is very characteristic. The latter compound converts the primary amines (better to act on the haloid salts with $AgNO_2$) into the corresponding alcohols (see p. 122):—

$$C_2H_5.NH_2 + NO.OH = C_2H_5.OH + N_2 + H_2O.$$

This is a reaction analogous in every respect to the decomposition of ammonium nitrite into water and nitrogen:—

$$NH_3 + NO.OH = H_2O + N_2 + H_2O.$$

Nitrous acid changes the secondary amines into nitroso-amines (p. 164):—

$$(CH_3)_2NH + NO.OH = \underset{\text{Nitroso-dimethylamine.}}{(CH_3)_2N.NO} + H_2O.$$

The tertiary amines remain intact or suffer decomposition. These reactions may also be employed to effect the separation of the amines.

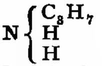
When aided by heat $KMnO_4$ breaks up the amines, nitrogen being eliminated and the alkyls being oxidized to aldehydes and acids (*Berichte*, 8, 1237).

Bromine in alkaline solution converts the primary amines (their HCl-salts) into alkylized nitrogen dibromides, *e. g.*, $C_2H_5.NBr_2$, the secondary amines at the same time throw off alkylen bromides and become primary amines (*Berichte*, 16, 558):—

$$(C_2H_5)_2NH + Br_2 = C_2H_5.NH_2 + C_2H_4Br_2.$$

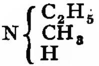
The alkalies change the bromides of the higher alkylamines into nitriles (p. 160). Well characterized compounds are those obtained by the action of dinitrochlorbenzene upon the primary and secondary amines (*Berichte*, 18, Ref. 540).

The possible isomerides of the amines are very numerous; they are determined not only by the isomerism of alcoholic radicals, but also by the number of replacing groups, as is manifest from the following examples:—



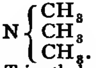
$$N\left\{\begin{matrix}C_3H_7\\ H\\ H\end{matrix}\right.$$

Propyl and Isopropylamine.



$$N\left\{\begin{matrix}C_2H_5\\ CH_3\\ H\end{matrix}\right.$$

Methyl-ethylamine.



$$N\left\{\begin{matrix}CH_3\\ CH_3\\ CH_3.\end{matrix}\right.$$

Trimethyl-amine.

They are thus distinguished: by the action of ethyl iodide the primary amines can receive two, the secondary, however, only one additional ethyl group, while the tertiary amines form ammonium bases directly. The power of forming carbylamines and mustard oils (see these) is especially characteristic of the primary amines; these are easily recognized by their odor (*Berichte*, **8**, 108 and 461).

PRIMARY AMINES.

Methylamine, $CH_3.NH_2$, is produced when the methyl ester of cyanic acid is heated with potash (p. 159); by the action of tin and hydrochloric acid upon chloropicrin, $CCl_3(NO_2)$; when nascent hydrogen acts upon hydrogen cyanide; and by the decomposition of various natural alkaloids, like theine, creatine, and morphine. The best way of preparing it is to warm brom-acetamide with caustic potash (see p. 159 and *Berichte*, **14**, 764):—

$$CH_3.CO.NHBr + 3KOH = CH_3.NH_2 + CO_3K_2 + KBr + H_2O.$$

Methylamine is a colorless gas, with an ammoniacal odor; it condenses to a liquid at —6°. Its combustibility in the air distinguishes it from ammonia. At 12° 1 volume of water dissolves 1150 volumes of the gas. The aqueous solution manifests all the properties of aqueous ammonia, but does not, however, dissolve the oxides of cobalt, nickel and cadmium. Iodine (also Br) throws out a dark red precipitate, $CH_3.NI_2$, from the solutions of methylamine:—

$$2CH_3.NH_2 + 2I_2 = CH_3.NI_2 + 2CH_3.NH_2.HI.$$

When methylamine is conducted over heated potassium it decomposes into potassium cyanide and hydrogen:—

$$CH_3.NH_2 + K = CNK + 5H.$$

The salts of methylamine are soluble in water. Its hydrochloride crystallizes in large, deliquescent leaflets, fusing at 100° and distilling without decomposition. It yields a yellow, crystalline, double salt—$[NH_2(CH_3)HCl]_2.PtCl_4$—with $PtCl_4$. Its double salt with auric chloride crystallizes in needles.

Ethylamine, $C_2H_5.NH_2$, is a mobile liquid, that boils at 18° and has a sp. gr. of 0.696 at 8°. It mixes with water in all proportions. It expels ammonia from ammoniacal salts, and when in excess redissolves aluminium hydroxide; otherwise it deports itself in every respect like ammonia.

Its hydrochloride, $NH_3(C_2H_5)Cl$, crystallizes in large, deliquescent leaflets, fusing at 80°. Its platinum double salt crystallizes in orange-red rhombohedra. Like ammonia, it also combines with $PtCl_2$ to form $PtCl_2(C_2H_5.NH_2)_2$. It exists as a white mass when in union with CO_2, and in this condition if added to a $BaCl_2$ solution it gradually precipitates barium carbonate. It probably corresponds to ammonium carbaminate.

β-Brom-Ethylamine, $CH_2Br.CH_2.NH_2$, is formed from brom-ethyl-phthalimide by the aid of HBr. Its hydrobromic acid salt melts at 155° (*Berichte*, 21, 566). Silver oxide or KOH converts the latter into vinylamine. For further derivatives consult *Berichte*, 22, 1139, 2222.

Propylamine, $C_3H_7.NH_2$, boils at 49°; **isopropylamine**, $C_3H_7.NH_2$, is most readily obtained by the reduction of dimethyl acetoxime, $(CH_3)_2C:N.OH$ (see p. 160); it boils at 31°–32°. (*Berichte*, 20, 505.)

Butylamine, $C_4H_9.NH_2$ (normal), boils at 76°; **isobutylamine**, $C_4H_9.NH_2$, obtained from fermentation butyl alcohol and from ordinary valeramide, boils at 66°.

Normal Amylamine, $C_5H_{11}.NH_2$, from normal caproylamide, $C_5H_{11}.CO.NH_2$, boils at 103°.

Isoamylamine, $C_5H_{11}.NH_2$, is a liquid boiling at 95°; it is obtained from leucine by distillation with caustic potash, or from isocaproylamide. It is miscible with water, and burns with a luminous flame. **Nonylamine**, $C_9H_{19}.NH_2$, obtained from normal caprylamide, boils about 195°, and is sparingly soluble in water. The higher alkylamines, containing an odd number of C-atoms, are most readily obtained by the action of sodium in alcoholic solution upon the nitriles of the fatty acids, $C_nH_{2n}.CN$—(see p. 159 and *Berichte*, 22, 812); while those with an even number of carbon atoms are produced by the action of bromine, in alkaline solution, upon the acid amides (p. 159 and *Berichte*, 21, 2486).

Vinylamine, $C_2H_3.NH_2$ (p. 134), results when silver oxide, or potassium hydroxide, acts upon bromethylamine. It is only known in solution. When evaporated with concentrated hydrochloric acid it yields chlorethylamine, $C_2H_4Cl.NH_2$. It forms taurine, $CH_3(NH_2).CH_3.SO_3H$, with sulphurous acid, amido-ethyl-sulphuric acid with H_2SO_4, and oxy-ethylamine, $CH_2.(NH_2).CH_2.OH$ (*Berichte*, 21, 2664) with water (by the action of nitric acid).

Allylamine, $C_3H_5.NH_2$, is obtained by the action of concentrated sulphuric acid, or zinc and hydrochloric acid, upon mustard oil ($C_3H_5.N:CS$); it is a liquid boiling at 58°.

Brom-allylamine, $C_3H_4Br.NH_2$ is obtained from the dibromide of allylamine. It boils at 125° (*Berichte*, 21, 3190.)

SECONDARY AMINES.

Dimethylamine, $NH(CH_3)_2$, is a gas that dissolves readily in water. It is condensed to a liquid by cold, and boils at 7.2°. It is most conveniently obtained by boiling nitroso-dimethyl aniline or dinitro-dimethyl aniline with caustic potash (*Annalen*, 222, 119). The platinum double salt crystallizes in large needles.

Diethylamine, $NH(C_2H_5)_2$, is a liquid boiling at 56° and is readily soluble in water. Its HCl-salt fuses at 216° and boils at 325°.

The secondary amines are also designated imide-bases.

Sulphamides, *e. g.*, $SO_2\left\langle\begin{matrix}N(CH_3)_2\\N(CH_3)_2\end{matrix}\right.$, are formed by the action of sulphuryl chloride, SO_2Cl_2, upon the free secondary amines, whereas their chlorides, $SO_2\left\langle\begin{matrix}NR_2\\Cl\end{matrix}\right.$, result when the HCl-salts are employed. Water converts the chlorides into sulphaminic acids, $SO_2\left\langle\begin{matrix}NR_2\\OH\end{matrix}\right.$ (*Annalen*, **222**, 118). SO_3 reacts similarly with the primary and secondary amines, forming mono- and dialkyl-sulphaminic acids (*Berichte*, **16**, 1265).

Nitroso-amines. These are compounds having the nitroso-group attached to N (p. 106). All basic secondary amines (imines), like $(CH_3)_2NH$ and $\left.\begin{matrix}C_6H_5\\C_2H_3O\end{matrix}\right\rangle NH$, can become nitroso-amines through the replacement of the hydrogen of the imide group. They are obtained from the free imides by the action of nitrous acid upon their aqueous, ethereal, or glacial acetic acid solutions, or by warming their salts in aqueous or acid solution with potassium nitrite (*Berichte*, **9**, 112). They are mostly oily, yellow liquids, insoluble in water, and may be distilled without suffering decomposition. Alkalies and acids are usually without effect upon them; with phenol and sulphuric acid they give the nitroso reaction (see p. 107). When reduced in alcoholic solution by means of zinc dust and acetic acid they become hydrazines (p. 166). Boiling hydrochloric acid decomposes them into nitrous acid, and dialkylamines.

Dimethyl Nitrosamine, $(CH_3)_2N.NO$, is a yellow oil, of penetrating odor. It boils at 148°.

Diethyl Nitrosamine, $(C_2H_5)_2N.NO$, is also an oil, boiling at 177°; it is obtained from HCl-diethylamine by distilling it with KNO_2 in aqueous solution. Concentrated hydrochloric acid regenerates diethylamine from it.

Nitroamines, containing the nitro-group in union with nitrogen, are produced by the action of concentrated nitric acid upon various amide derivatives (*Berichte*, **18**, Ref. 146; **22**, Ref. 295).

Methyl-nitramine, $CH_3.NH(NO_2)$, from the esters of methyl carbaminate, melts at 38°. It has an acid reaction. **Ethyl-nitramine**, $C_2H_5.NH(NO_2)$, from ethyl carbaminate, solidifies on cooling, and melts at 3°. **Dimethyl-nitramine**, $(CH_3)_2.N(NO_2)$, is formed by the action of potassium hydroxide and methyl iodide upon methylnitramine. It melts at 58°, and boils at 187° (*Berichte*, **22**, Ref. 296).

TERTIARY AMINES.

Trimethylamine, $N(CH_3)_3$. This is isomeric with propylamine, $C_3H_7.NH_2$, and is present in herring-brine; it is produced by distilling betaïne (from the beet) with caustic potash. It is prepared from herring-brine in large quantities, and also by the distillation of the "vinasses" of the French beet root. Trimethylamine is a liquid, very soluble in water, and boils at 3.5°. The penetrating, fish-like smell is characteristic of it. Its HCl-salt is very deliquescent.

Triethylamine, $N(C_2H_5)_3$, boils at 89° and is not very soluble in water. It is produced by heating ethyl isocyanate with sodium ethylate:—$CO{:}N.C_2H_5 + 2C_2H_5.ONa = N(C_2H_5)_3 + CO_3Na_2$.

AMMONIUM BASES.

The tertiary amines combine with alkyl iodides and yield ammonium iodides; these are scarcely affected by the alkalies, even on boiling (p. 158); but when treated with moist silver oxide the *ammonium hydroxides* are formed:—

$$N(C_2H_5)_4I + AgOH = N(C_2H_5)_4.OH + AgI.$$

These hydroxides are perfectly analogous to those of potassium and sodium. They possess strong alkaline reaction, saponify fats, and deliquesce in the air. They crystallize when their aqueous solutions are concentrated in vacuo. With the acids they yield ammonium salts; these usually crystallize well.

On exposure to strong heat they break up into tertiary amines and alcohols, or their decomposition products (C_nH_{2n} and H_2O):—

$$N(C_2H_5)_4.OH = N(C_2H_5)_3 + C_2H_4 + H_2O.$$

If the ammonium base contains different alkyls, it is usually the ethyl group that is split off (*Berichte*, 14, 494).

If iodine is added to the aqueous solution of the iodides, compounds are precipitated which contain three and five atoms of iodine: $(C_2H_5)_4NI.I_2$ and $(C_2H_5)_4NI.2I_2$.

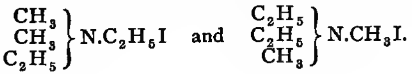
The tri-iodides are mostly dark violet bodies; the penta-iodides resemble iodine very much.

Tetraethyl Ammonium Iodide, $N(C_2H_5)_4I$, is obtained by mixing triethylamine with ethyl iodide; the mixture becomes warm and when it cools is crystalline. It separates from water or alcohol in large prisms, that fuse when heated, and then decompose into $N(C_2H_5)_3$ and C_2H_5I. Moist silver oxide converts it into

Tetraethyl Ammonium Hydroxide, $N(C_2H_5)_4OH$, which crystallizes in delicate, deliquescent needles. It absorbs CO_2 from the air with avidity. Its platinum double salt, $[N(C_2H_5)_4Cl]_2.PtCl_4$, crystallizes in octahedrons.

Tetraethyl Ammonium Cyanide, $(C_2H_5)_4N.CN$, is a white, crystalline mass. It is obtained by acting on the hydroxide with HCN, or upon the iodide with barium cyanide. When boiled with alkalies it decomposes into NH_3, formic acid and ammonium hydroxide.

Dimethyl-diethyl Ammonium Chloride, $\left.\begin{matrix}(CH_3)_2\\(C_2H_5)_2\end{matrix}\right\}NCl$, is obtained from dimethylamine and ethyl iodide, and from diethylamine and methyl iodide:—



$$\left.\begin{matrix}CH_3\\CH_3\\C_2H_5\end{matrix}\right\}N.C_2H_5I \quad\text{and}\quad \left.\begin{matrix}C_2H_5\\C_2H_5\\CH_3\end{matrix}\right\}N.CH_3I.$$

These two compounds are identical (*Annalen*, **180**, 273). They demonstrate, too, that the ammonium compounds are not molecular derivatives as formerly assumed (the above formulas are only intended to exhibit the different manner of formation), but represent true atomic compounds. They further show the equivalence of the five nitrogen valences (compare Le Bel, *Berichte*, **23**, Ref. 147).

HYDROXYLAMINE DERIVATIVES.

The amines are derived from ammonia. Hydroxylamine also yields a series of analogous alkyl compounds, very similar to the amines. The entrance of one alkyl group produces two isomeric forms:—

(α) $NH_2.O.CH_3$ Hydroxylamine Ether. and (β) $CH_3.NH.OH$. Alkyl Hydroxylamine.

The derivatives of the first modification are also called *Alkylhydroxylamines.* They result from the decomposition of the ethers of α-benzaldoxime, *e. g.*, $C_6H_5.CH:N.O.CH_3$, on digesting them with acids, or from the esters of ethylbenzhydroxamic acid (see this) (*Berichte*, **16**, 827; **22**, Ref. 587). The β-alkylhydroxylamines seem to be similarly derived from the ethers of β-benzaldoxime (*Berichte*, **23**, 599).

α-Methylhydroxylamine, $NH_2.O.CH_3$, *Methoxylamine*, prepared by the first two methods, yields an HCl-salt, which melts at 149°. It differs from hydroxylamine in that it does not reduce alkaline copper solutions.

β-Methylhydroxylamine, $CH_3.NH.OH$(?), from the methyl ether of β-isobenzaldoxime, forms an HCl-salt, melting at 85–90°.

α-Ethylhydroxylamine, $NH_2.O.C_2H_5$(?), *Ethoxylamine*, derived from ethylbenzhydroxamate, is a liquid, boiling at 68°. The compound obtained from ethylbenzaldoxime has not been accurately studied (*Berichte*, **16**, 829).

The action of ethyl bromide upon ethoxylamine produces *Diethylhydroxylamine*, $C_2H_5.NH.O.C_2H_5$, and *Triethylhydroxylamine*, $(C_2H_5)_2.N.O.C_2H_5$, boiling at 98° (*Berichte*, **22**, Ref. 590). An isomeride of the latter has been prepared by the interaction of zinc ethide and nitro-ethane. It boils at 155° (*Berichte*, **22**, Ref. 250).

HYDRAZINES.

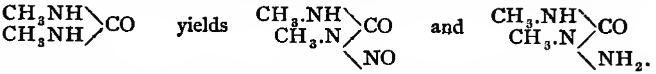
Just as the *amines* are derived from ammonia, NH_3, so the hydrazines are derived from *hydrazine* or *diamide*, $H_2N — NH_2$, an analogue of liquid hydrogen phosphide, $H_2P — PH_2$, and dimethylarsine (cacodyl), $(CH_3)_2As — As(CH_3)_2$.

The preparation of hydrazine in a free state is of recent date. It has been obtained from diazo-acetic acid (see this). Its derivatives, however, have been known for quite a long time, and have been prepared by a variety of methods. They hold an important place in the benzene series (see phenyl hydrazine, $C_6H_5.NH.NH_2$) (E. Fischer, *Annalen*, 99, 281).

The mono- and dialkyl hydrazines are at present the only known derivatives.

In physical and chemical properties they closely resemble the amines, but are distinguished from them by their ability to reduce alkaline copper solutions. They are powerful bases, uniting with one and two equivalents of acids to form salts.

The mono-alkyl hydrazines are obtained from the mono-alkyl ureas, $NH_2.CO.NH.R$, and from the symmetrical dialkylureas by their conversion into nitroso-compounds, and the reduction of the latter to hydrazines of the ureas:—



$$\begin{matrix}CH_3NH\\CH_3NH\end{matrix}\!\!>CO \quad \text{yields} \quad \begin{matrix}CH_3.NH\\CH_3.N\\ \quad\diagdown NO\end{matrix}\!\!>CO \quad \text{and} \quad \begin{matrix}CH_3.NH\\CH_3.N\\ \quad\diagdown NH_2.\end{matrix}\!\!>CO$$

When the latter are heated with alkalies or acids they split up, like all urea derivatives, into their components, CO_2, alkylamine and alkylhydrazine.

Methyl Hydrazine, $CH_3.NH.NH_2$, from methyl urea, is a very mobile liquid, boiling at 87°. Its odor is like that of methylamine. In the air it absorbs moisture and fumes (*Berichte*, 22, Ref. 670).

Ethyl Hydrazine, $(C_2H_5)HN.NH_2$, obtained from diethyl urea, is perfectly similar to the methyl derivative. It boils at 100°. Both compounds reduce Fehling's solution in the cold.

When ethyl hydrazine is acted upon by potassium disulphate, and the product treated with monopotassium carbonate, *potassium ethyl hydrazine sulphonate*, $C_2H_5.NH—NH.SO_3K$, is formed. Mercuric oxide changes this to *potassium diazo-ethyl sulphonate*, $C_2H_5.N=N.SO_3K$. This is the only well-known representative in the fatty-series of a numerous and highly important class of derivatives of the benzene series—the *diazo-compounds*. They are characterized by the *diazo group*,—N=N—, which is in union with carbon radicals.

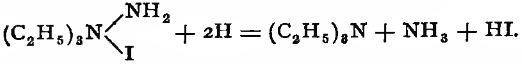
Dialkylhydrazines, like $(CH_3)_2N.NH_2$, are formed by the reduction of nitroso-amines, in aqueous and alcoholic solution, by zinc dust and acetic acid:—

$$(CH_3)_2N.NO + 2H_2 = (CH_3)_2N.NH_2 + H_2O.$$

Nitroso-amines containing at the same time acid radicals, *e.g.*, $\begin{matrix}C_6H_5\\C_2H_3O\end{matrix}\!\!>N.NO$, do not yield corresponding hydrazines, but revert to amides.

Dimethyl Hydrazine, $(CH_3)_2N.NH_2$, and **Diethyl Hydrazine**, $(C_2H_5)_2N.NH_2$, are mobile liquids, of ammoniacal odor, and readily soluble in water, alcohol and ether. Diethyl hydrazine boils at 97°, and the dimethyl compound at 62°. They reduce Fehling's solution when warm.

Diethylhydrazine unites with ethyl iodide and yields the compound $(C_2H_5)_2.N.NH_2.C_2H_5I$, which is to be viewed as the *ammonium iodide*, $(C_2H_5)_3\overset{v}{N}\begin{matrix}\diagup NH_2\\ \diagdown I,\end{matrix}$ as it is not decomposed by alkalies, and moist silver oxide converts it into a strong alkaline hydroxide. Nascent hydrogen (zinc and sulphuric acid) decomposes this iodide in the manner indicated in the following equation:—



$$(C_2H_5)_3N\begin{matrix}\diagup NH_2\\ \diagdown I\end{matrix} + 2H = (C_2H_5)_3N + NH_3 + HI.$$

This reaction is an additional proof that the ammonium compounds represent atomic derivatives of pentavalent nitrogen (*Annalen*, 199, 318). When mercuric oxide acts upon diethylhydrazine *tetrazone*, $(C_2H_5)_2N.N:N.N(C_2H_5)_2$, is formed. This is a strong basic liquid with an alliaceous odor.

PHOSPHINES OR PHOSPHORUS BASES.

Hydrogen phosphide, PH_3, has slight basic properties. Its compound with HI—phosphonium iodide, PH_4I—is not very stable. Through the introduction of alkyls (alcohol radicals), it acquires the strong basic character of ammonia; its derivatives—the phosphines or phosphorus bases—correspond perfectly to the amines.

When the alkyl iodides act upon phosphine, tertiary phosphines and phosphonium iodides (Thénard) are the sole products:—

$$PH_3 + 3C_2H_5I = P(C_2H_5)_3.HI + 2HI, \text{ and}$$
$$P(C_2H_5)_3 + C_2H_5I = P(C_2H_5)_4I.$$

It was A. W. Hofmann (1871) who prepared the *primary* and *secondary* derivatives by letting the alkyl iodides act upon phosphonium iodide in the presence of certain metallic oxides, chiefly zinc oxide, the mixture being at the same time heated to about 150°. This procedure yields a mixture of the two classes (their HI salts):—

$$2PH_4I + 2C_2H_5I + ZnO = 2P(C_2H_5)H_2.2HI + ZnI_2 + H_2O, \text{ and}$$
$$PH_4I + 2C_2H_5I + ZnO = P(C_2H_5)_2H.HI + ZnI_2 + H_2O.$$

Water releases the monophosphine from the crystalline mass:—

$$P(C_2H_5)H_3I + H_2O = P(C_2H_5)H_2 + HI + H_2O.$$

This is like the decomposition of PH_4I by water into PH_3 and HI. The HI salt of the diethylphosphine is not affected. But by boiling the latter with sodium hydroxide, diethylphosphine is set free.

Thénard (1846) first discovered the tertiary phosphines by acting upon calcium phosphide with alkyl iodides. They also result when zinc alkyls are brought in contact with phosphorous chloride:—

$$2PCl_3 + 3(CH_3)_2Zn = 2P(CH_3)_3 + 3ZnCl_2,$$

and upon heating the alkyl iodides to 100° with amorphous phosphorus. The easiest course is to heat phosphonium iodide with alkyl iodides to 150°–180°, whereby phosphonium iodides are produced at the same time:—

$$PH_4I + 3CH_3I = P(CH_3)_3.HI + 3HI, \text{ and}$$
$$P(CH_3)_3HI + CH_3I = P(CH_3)_4I + HI.$$

If these be digested with potassium hydroxide, the tertiary phosphine is eliminated, while the iodide of the phosphonium base is unaltered (the case with the amines).

The phosphines are colorless, strongly refracting, extremely powerful-smelling, volatile liquids. They are nearly insoluble in water. On exposure to the air they are energetically oxidized and usually inflame spontaneously; hence, they must be prepared away from air contact. They combine readily with sulphur and carbon disulphide. They form salts with the acids. Primary phosphines are very slightly basic, therefore, water decomposes their salts (see above).

PRIMARY PHOSPHINES.

Methyl Phosphine, $P(CH_3)H_2$, is a gas, condensing at — 20° to a mobile liquid. It is readily soluble in alcohol and ether. Concentrated hydrochloric acid does not decompose its HCl-salt, $P(CH_3)H_2.HCl$. It yields a double salt with platinic chloride. Fuming nitric acid oxidizes it to methyl phosphinic acid, $CH_3.PO.(OH_2)$ (p. 156).

Ethyl Phosphine, $P(C_2H_5)H_2$, boils at + 25° and swims upon water. It is very energetically oxidized by air contact, and ignites when brought near chlorine and bromine. Its platinum double salt consists of red needles.

Isopropyl Phosphine, $P(C_3H_7)H_2$, boils at 41°, and the **isobutyl** derivative, $P(C_4H_7)H_2$, at 62°.

SECONDARY PHOSPHINES.

Dimethyl Phosphine, $P(CH_3)_2H$, boils at 25° C., and takes fire on exposure to the air. Concentrated nitric acid converts it into dimethyl phosphinic acid, $(CH_3)_2PO.OH$ (p. 156).

Diethyl Phosphine, $P(C_2H_5)_2H$, boils at 85° and inflames spontaneously. Nitric acid oxidizes it to diethyl phosphinic acid $(C_2H_5)_2PO.OH$.

Di-isopropyl Phosphine, $P(C_3H_7)_2H$, boils at 118°. **Di-isoamyl Phosphine,** $P(C_5H_{11})_2H$, boils at 210°–215°, fumes in the air, but is not self-inflammable.

Water does not decompose the salts of the secondary phosphines. The HI salts and the double salts with platinic chloride are prepared with the least difficulty.

TERTIARY PHOSPHINES.

Trimethyl Phosphine, $P(CH_3)_3$, is prepared by heating carbon disulphide with phosphonium iodide. It is a colorless, very disagreeably smelling liquid, which will swim upon water. It boils at 40°. It fumes in the air, absorbing oxygen and igniting. When slowly oxidized it changes to trimethyl phosphine oxide, $P(CH_3)_3O$, which forms crystals that are deliquescent in the air. Sulphur will dissolve in the base and give a crystalline sulphide, $P(CH_3)_3S$. It combines in a like manner with the halogens, their hydrides, and also with CS_2. It yields salts with the acids; these are very soluble in water.

Triethyl Phosphine, $P(C_2H_5)_3$, is analogous to the above compound. It boils at 117°, and has a specific gravity of 0.812 at 15°. It has a neutral reaction. It dissolves slowly in acids, yielding salts. Its platinum double salt, $[P(C_2H_5)_3HCl]_2.PtCl_4$, is sparingly soluble in water and crystallizes in red needles. It forms crystalline halogen derivatives, $P(C_2H_5)_3X_2$.

Triethyl Phosphine Oxide, $P(C_2H_5)_3O$, results from the slow oxidation of phosphine in the air, and by the action of mercuric oxide:—

$$P(C_2H_5)_3 + HgO = P(C_2H_5)_3O + Hg.$$

It forms deliquescent needles, melting at 53°, and distilling without decomposition at 243°. With the haloid acids it yields dihaloids, *e. g.*, $P(C_2H_5)_3Cl_2$ from which triethyl phosphine is produced on warming with sodium.

Triethyl phosphine dissolves sulphur to form a sulphide, $P(C_2H_5)_3S$, which crystallizes from water in brilliant needles, fusing at 94° and distilling about 100°. Mercury or lead oxide converts it into the oxide. Carbon disulphide also combines with triethyl phosphine, and the product is $P(C_2H_5)_3.CS_2$, crystallizing in red leaflets. It is insoluble in water, fuses at 95°, and sublimes without decomposition.

According to almost all these reactions, triethyl phosphine resembles a strongly positive bivalent metal; for example, calcium. By the addition of three alkyl groups, the pentavalent, metalloidal phosphorus atom acquires the character of a bivalent alkaline earth metal. By the further addition of an alkyl to the phosphorus in the phosphonium group, $P(CH_3)_4$, the former acquires the properties of a monovalent alkali metal. Similar conditions manifest themselves with sulphur, with tellurium, with arsenic, and also with almost all the less positive metals.

PHOSPHONIUM BASES.

The tertiary phosphines combine with the alkyl iodides to form phosphonium iodides, not decomposed by alkalies:—

$$P(CH_3)_3 + CH_3I = P(CH_3)_4I.$$

If, however, the iodides be treated with moist silver oxide the *phosphonium bases* result:—

$$P(CH_3)_4I + AgOH = P(CH_3)_4.OH + AgI.$$

These are perfectly analogous to the ammonium bases; they react alkaline, absorb carbon dioxide, and saturate the acids to form salts. When strongly heated they break up into phosphine oxide and hydrocarbons of the paraffin series:—

$$P(CH_3)_4.OH = P(CH_3)_3O + CH_4.$$

Tetraethyl Phosphonium Iodide, $P(C_2H_5)_4I$, consists of very soluble, white needles. When heated these decompose into $P(C_2H_5)_3$ and C_2H_5I.

Tetraethyl Phosphonium Hydroxide, $P(C_2H_5)_4.OH$, is a crystalline compound that deliquesces on exposure. With acids it forms crystalline salts. The platinum double salt crystallizes in orange-red octahedra.

ARSENIC BASES.

Arsenic is quite metallic in its character; its alkyl compounds constitute the transition from the nitrogen and phosphorus bases to the so-called metallo-organic derivatives, *i. e.*, the compounds of the alkyls with the metals (p. 177). The similarity to the amines and phosphines is observed in the existence of tertiary arsines, $As(CH_3)_3$, but these do not possess basic properties, nor do they unite with acids. They show in a marked degree the property of the tertiary phosphines, in their uniting with oxygen, sulphur and the halogens, to form compounds of the type $As(CH_3)_3X_2$. They yield *arsonium iodides* with the alkyl iodides:—

$$As(CH_3)_3 + CH_3I = As(CH_3)_4I,$$

and these in turn become *hydroxides* by the action of moist silver oxide:—

$$As(CH_3)_4I + AgOH = As(CH_3)_4.OH + AgI.$$

These hydroxides are analogous to the ammonium and phosphonium bases; they are very alkaline and yield salts with acids.

The arsines analogous to the *primary* and *secondary* amines and phosphines, such as $As(CH_3)H_2$ and $As(CH_3)_2H$, are unknown, and probably cannot exist. Through an accumulation of alkyls, arsenic, like the metals, receives a more positive character; $As(CH_3)_2Cl$ and $As(CH_3)Cl_2$ act like the chlorides of the more positive metals.

By the acquisition of two halogen atoms the compounds of the form AsX_3 pass into AsX_5:—

$$\begin{array}{lll} As(CH_3)_3 & \text{yields} & As(CH_3)_3Cl_2 \\ As(CH_3)_2Cl & \text{“} & As(CH_3)_2Cl_3 \\ As(CH_3)Cl_2 & \text{“} & As(CH_3)Cl_4. \end{array}$$

Heat converts these into the compounds of the form AsX_3 and alkylogens:—

$$\begin{aligned} As(CH_3)_4Cl &= As(CH_3)_3 + CH_3Cl \\ As(CH_3)_3Cl_2 &= As(CH_3)_2Cl + CH_3Cl \\ As(CH_3)_2Cl_3 &= As(CH_3)Cl_2 + CH_3Cl \text{ and} \\ As(CH_3)Cl_4 &= AsCl_3 + CH_3Cl. \end{aligned}$$

The readiness with which these compounds are decomposed increases with the accumulation of the halogen atoms, *e. g.*, $As(CH_3)Cl_4$ breaks up at 0°, while $AsCl_5$ has not been obtained.

TERTIARY ARSINES AND ARSONIUM COMPOUNDS.

The tertiary arsines are formed by the action of the zinc alkyls upon arsenic trichloride:—

$$2AsCl_3 + 3Zn(CH_3)_2 = 2As(CH_3)_3 + 3ZnCl_2;$$

and by heating the alkyl iodides with sodium arsenide:—

$$AsNa_3 + 3C_2H_5I = As(C_2H_5)_3 + 3NaI.$$

Cacodyl, formed simultaneously, is separated by fractional distillation.

Trimethylarsine, $(CH_3)_3As$, is a colorless liquid, insoluble in water, and boils below 100° C. Its odor is very disagreeable. It fumes in the air, and absorbs oxygen, to form the oxides, $As(CH_3)_3O$, consisting of large deliquescent crystals. It also unites with the halogens and sulphur, forming $As(CH_3)_3Br_2$ and $As(CH_3)_3S$, soluble in water. At ordinary temperatures it combines with methyl iodide, forming **tetramethyl-arsonium iodide**, $As(CH_3)_4I$, which crystallizes from water in brilliant tables. Heat decomposes this last derivative into $As(CH_3)_3$ and CH_3I. By the action of moist silver oxide **tetramethyl-arsonium hydroxide**, $As(CH_3)_4.OH$, is obtained. This substance has a strongly alkaline reaction, is deliquescent, expels ammonia from its salts, and yields crystalline salts with the acids.

Triethylarsine, $As(C_2H_5)_3$, is a liquid sparingly soluble in water, and boiling at 140°, with partial decomposition. It fumes in the air, but only takes fire when heated. From its ethereal solution iodine precipitates the iodide, $As(C_2H_5)_3I_2$, a yellow amorphous substance. The oxide, $As(C_2H_5)_3O$, is a heavy oil, of disagreeable odor. It seems to combine to a salt with nitric acid. The sulphide, $As(C_2H_5)_3S$, is a crystalline substance, soluble in water.

Tetraethyl-arsonium Iodide, $As(C_2H_5)_4I$, is produced by the union of triethyl-arsine and ethyl iodide. It is a crystalline compound, which forms an **hydroxide**, $As(C_2H_5)_4.OH$, when treated with silver oxide. This is a strongly basic, deliquescent body, yielding salts with the acids. The platinum double salt consists of sparingly soluble, orange-red crystals.

DIMETHYLARSINE COMPOUNDS.

The monovalent group, $As(CH_3)_2$, is strongly basic (see p. 171), and can form a series of derivatives, which, owing to their extremely disgusting odor, have been termed *cacodyl compounds* (from *κακός* and *ὀδεῖν*):—

$As(CH_3)_2Cl$	Cacodyl Chloride.	$\begin{matrix}As(CH_3)_2\\ \vert\\ As(CH_3)_2\end{matrix}$	Free Cacodyl.
$\begin{matrix}As(CH_3)_2\\As(CH_3)_2\end{matrix}>O$	Cacodyl Oxide.	$As(CH_3)_2.CN$	Cacodyl Cyanide.
$\begin{matrix}As(CH_3)_2\\As(CH_3)_2\end{matrix}>S$	Cacodyl Sulphide.	$\overset{v}{As}(CH_3)_2O.OH$	Cacodylic Acid.

Cacodyl Chloride, $As(CH_3)_2Cl$, is formed by heating trimethyl arsendichloride, $As(CH_3)_3Cl_2$ (see above), and by acting upon cacodyl oxide with hydrochloric acid. It is more readily obtained by heating the corrosive sublimate compound of the oxide with hydrochloric acid. It is a colorless liquid, boiling at about 100°, and possessing a stupefying odor. It acts like a chloride of the alkali metals, and yields an insoluble double salt with $PtCl_4$. It unites with chlorine to form the *trichloride*, $As(CH_3)_2Cl_3$, which decomposes at 50° into $As(CH_3)Cl_2$ and CH_3Cl.

The bromide and iodide, $As(CH_3)_3I$, resemble the chloride, and are prepared in an analogous way.

Cacodyl, $As_2(CH_3)_4 = \begin{matrix}As(CH_3)_2\\ \vert\\ As(CH_3)_2\end{matrix}$, diarsentetramethyl, is formed by heating the chloride with zinc filings in an atmosphere of CO_2. It is a colorless liquid, insoluble in water. It boils at 170°, and solidifies at —6°. Its odor is frightfully strong, and may induce vomiting. Cacodyl takes fire very readily in the air and burns to As_2O_3, carbon dioxide and water. It yields cacodyl chloride with chlorine and the sulphide with sulphur. Nitric acid converts it into a nitrate, $As(CH_3)_2.O.NO_2$.

Cacodyl Oxide, $\left.\begin{matrix}As(CH_3)_2\\As(CH_3)_2\end{matrix}\right\rangle O$, also termed *alcarsin*, is most easily made by distilling arsenic trioxide with potassium acetate:—

$$4CH_3.CO_2K + As_2O_3 = \left.\begin{matrix}As(CH_3)_2\\As(CH_3)_2\end{matrix}\right\rangle O + 2CO_3K_2 + 2CO_2.$$

The distillate ignites spontaneously, because it contains some free cacodyl; the pure oxide does not act in this way.

Cacodyl oxide is a liquid with stupefying odor; it boils at 150°, and at — 25° solidifies to a scaly mass; its specific gravity at 15° is 1.462. It is insoluble in water, but dissolves very readily in alcohol and ether. It unites with acids to form salts; these are purified with great difficulty. The sulphate appears to have the formula:—

$$SO_2\left\langle\begin{matrix}O.As(CH_3)_2\\O.As(CH_3)_2\end{matrix}\right..$$

Slow oxidation converts the oxide into **cacodyl cacodylate,** which breaks up when distilled with H_2O into the oxide and cacodylic acid:—

$$\left.\begin{matrix}As(CH_3)_2\\2As(CH_3)_2O\end{matrix}\right\rangle O + H_2O = [As(CH_3)_2]_2O + 2As(CH_3)_2O.OH.$$

Cacodyl Sulphide, $\left.\begin{matrix}As(CH_3)_2\\As(CH_3)_2\end{matrix}\right\rangle S$, is obtained by distilling cacodyl chloride with barium sulphide. It is an oily liquid insoluble in water, and inflames in the air. Hydrochloric acid decomposes it into cacodyl chloride and H_2S. Sulphur dissolves in both it and cacodyl, forming the *disulphide*, $[As(CH_3)_2]_2S_2$, crystallizing in rhombic tables, fusing at 50°.

Cacodyl Cyanide, $As(CH_3)_2.CN$, is formed by heating cacodyl chloride with mercuric cyanide, or by the action of CNH upon cacodylic oxide. It crystallizes in glistening prisms, which fuse at 37°, and boil at 140°.

Cacodylic Acid, $(CH_3)_2AsO.OH$ (see p. 156), (dimethyl-arsinic acid), is obtained by the action of mercuric oxide upon cacodylic oxide:—

$$\left.\begin{matrix}As(CH_3)_2\\As(CH_3)_2\end{matrix}\right\rangle O + 2HgO + H_2O = 2As(CH_3)_2O.OH + 2Hg.$$

It is easily soluble in water, and crystallizes in large prisms, which melt at 200°, with partial decomposition. Cacodylic acid is odorless, and appears to be non-poisonous. Its solution reacts acid, and forms crystallizable salts with the metallic oxides, *e.g.*, $(CH_3)_2AsO.OAg$.

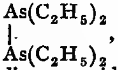
Hydriodic acid reduces the acid to iodide:—

$$As(CH_3)_2O.OH + 3HI = As(CH_3)_2I + 2H_2O + I_2.$$

Hydrogen sulphide changes it to sulphide.

The salts of the thio-cacodylic acid, $(CH_3)_2AsS.SH$, corresponding to cacodylic acid, are formed by the action of salts of the heavy metals upon cacodyl disulphide.

There are ethyl compounds analogous in constitution to the preceding methyl derivatives, but they have not been well investigated.

Ethyl Cacodyl,  $\begin{matrix} As(C_2H_5)_2 \\ | \\ As(C_2H_5)_2 \end{matrix}$, diethylarsine, is formed together with triethylarsine on heating sodium arsenide with ethyl iodide. It is an oil, boiling at 185–195°, and takes fire in the air. When its alcoholic solution is permitted to slowly oxidize in the air, *diethyl arsinic acid,* $(C_2H_5)_2AsO.OH$ (see p. 156), is produced; this crystallizes in deliquescent leaflets.

MONOMETHYL ARSINE COMPOUNDS.

Methylarsen-Dichloride, $As(CH_3)Cl_2$, results in the decomposition of cacodylic acid with hydrochloric acid:—

$$As(CH_3)_2O.OH + 3HCl = As(CH_3)Cl_2 + CH_3Cl + 2H_2O.$$

It is a heavy liquid, soluble in water, and boils at 133°. At —10° it unites with chlorine, forming $As(CH_3)Cl_4$, which at 0° breaks up into $AsCl_3$ and CH_3Cl. From the alcoholic solution hydrogen sulphide precipitates the *sulphide,* $As(CH_3)S$, crystallizing in colorless needles, melting at 110°.

When sodium carbonate acts upon the aqueous solution of the dichloride *methyl-arsenoxide,* $As(CH_3)O$, is formed. This is soluble, with difficulty, in water, and crystallizes from alcohol in colorless prisms, which fuse at 95°, and distil along with steam. The oxide is basic, and may be converted by the haloid acids and H_2S into the halogen derivatives, $AsCH_3X_2$, and the sulphide, $AsCH_3S$.

Silver oxide acting upon the aqueous solution of the above oxide changes it into the silver salt of mono-methyl arsinic acid, $(CH_3)AsO(OH)_2$, an analogue of methyl phosphinic acid (p. 156). The free acid crystallizes in large plates, reacts acid, expels CO_2 from carbonates, and combines with bases to yield salts, like $(CH_3)AsO(O.Ag)_2$. Phosphorus pentachloride converts it into $As(CH_3)Cl_2$. When ethyl iodide acts upon sodium arsenite, AsO_3Na_3 (p. 152), sodium mono-ethyl arsinate, $C_2H_5.AsO(ONa)_2$, is produced.

ANTIMONY COMPOUNDS.

The derivatives of antimony and the alkyls are perfectly analogous to those of arsenic; but those containing one and two alkyl groups do not exist.

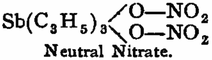
Trimethylstibine, $Sb(CH_3)_3$, antimony trimethyl, is obtained by heating methyl iodide with an alloy of antimony and potassium. It is a heavy liquid, insoluble in water, fuming and also taking fire in the air. It boils at 80°. It dissolves with difficulty in alcohol, but readily in ether. It forms compounds similar to those of triethyl stibine with the halogens and with oxygen. Antimony pentamethyl, $Sb(CH_3)_5$, is formed when zinc methyl is permitted to act upon trimethyl stibine di-iodide. It is a liquid, and boils at about 100°. It does not ignite spontaneously.

Methyl iodide and trimethyl stibine unite, and yield *tetramethylstibonium iodide,* $Sb(CH_3)_4I$, which crystallizes from water in beautiful tables. Digested with moist silver oxide it passes into the hydroxide, $Sb(CH_3)_4.OH$,—a deliquescent, crystalline mass with strong alkaline reaction. The hydroxide forms beautifully crystallized salts with acids.

Triethylstibine or Stibethyl, $Sb(C_2H_5)_3$. This is perfectly analogous to the methyl derivative. In all its reactions it manifests the character of a bivalent metal, perhaps calcium or zinc (see p. 170). With oxygen, sulphur, and the halogens, it combines energetically and decomposes the concentrated haloid acids, expelling their hydrogen:—

$$Sb(C_2H_5)_3 + 2HCl = Sb(C_2H_5)_3Cl_2 + H_2.$$

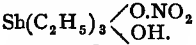
The dichloride, $Sb(C_2H_5)_3Cl_2$, is a thick liquid, having an odor like that of turpentine. The *bromide* solidifies at —10°; the *iodide* crystallizes in needles, fusing at 70°. Stibethyl slowly oxidized in the air becomes *triethylstibine oxide*, $Sb(C_2H_5)_3O$, an amorphous solid, soluble in water. It behaves like a di-acidic oxide, forming basic and neutral salts, which crystallize well, *e. g.*:—



$$Sb(C_3H_5)_3\begin{cases}O—NO_2\\O—NO_2\end{cases}$$

Neutral Nitrate.

and



$$Sb(C_2H_5)_3\begin{cases}O.NO_2\\OH.\end{cases}$$

Basic Nitrate.

Triethylstibine Sulphide, $Sb(C_2H_5)_3S$, is formed by the union of stibethyl and sulphur. It consists of shining crystals, melting at about 100°. It behaves somewhat like calcium sulphide. It dissolves readily in water, precipitates sulphides from solutions of the heavy metals and is decomposed by acids with the formation of hydrogen sulphide and salts of triethylstibine oxide.

Tetraethylstibonium Iodide, $Sb(C_2H_5)_4I$, is obtained from ethyl iodide and triethylstibine. It separates from water in large prisms. Silver oxide converts the iodide into *tetraethylstibonium hydroxide*, $Sb(C_2H_5)_4.OH$, a thick liquid, reacting strongly alkaline, and yielding well crystallized salts with acids.

BORON COMPOUNDS.

Triethylborine, or Borethyl, $B(C_2H_5)_3$, is formed by the action of zinc ethyl upon boric ethyl ester (p. 155):—

$$2B(O.C_2H_5)_3 + 3Zn(C_2H_5)_2 = 2B(C_2H_5)_3 + 3(C_2H_5.O)_2Zn.$$

It is a colorless, mobile liquid, of penetrating odor; its boiling point is 95°, and its sp. gr. at 23° equals 0.696. It ignites in contact with the air and burns with a green flame. When heated together with hydrochloric acid it decomposes into diethylborine chloride and ethane:—

$$B(C_2H_5)_3 + HCl = B(C_2H_5)_2Cl + C_2H_6.$$

Slowly oxidized in the air triethylborine passes into the diethyl ester of ethyl boric acid or **Boron Etho-diethoxide,** $B(C_2H_5)(O.C_2H_5)_2$. This is a liquid boiling at 125°; water decomposes it into alcohol and ethyl boric acid, $C_2H_5.B(OH)_2$. The latter is a crystalline, volatile body, which has a faintly acid reaction and is soluble in water, alcohol and ether.

Bormethyl, trimethylborine, $B(CH_3)_3$, is a colorless gas, that may be condensed by cold.

SILICON COMPOUNDS.

The nearest analogue of carbon is silicon, therefore its derivatives with alcoholic radicals are very similar to the hydrocarbons.

Silicon-methyl, $Si(CH_3)_4$, is formed on heating $SiCl_4$ with zinc methyl:—

$$SiCl_4 + 2Zn(CH_3)_2 = Si(CH_3)_4 + 2ZnCl_2.$$

It is a mobile liquid, boiling at 30°. It is not changed by water, boils at + 10°, and behaves like a hydrocarbon (carbon tetramethane, $C(CH_3)_4$).

Silicon-Ethyl, Silicon-Tetraethide, $Si(C_2H_5)_4$, is similar to the preceding, and boils at 153°. By the action of chlorine there is formed a substitution product, $Si\left\{\begin{matrix}(C_2H_5)_3\\ C_2H_4Cl\end{matrix}\right.$, boiling at 185°, which acts exactly like a chloride of a hydrocarbon. By the action of potassium acetate on this an acetic ester results:—

$$(C_2H_5)_3\overset{IV}{Si}.C_2H_4.O.C_2H_3O.$$

Alkalies decompose this into acetic acid and the alcohol:—

$$(C_2H_5)_3\overset{IV}{Si}.C_2H_4.OH.$$

This so-called **silico-nonyl alcohol** corresponds to nonyl alcohol, $(C_2H_5)_3C.CH_2.CH_2OH$. It boils at 195°, and is insoluble in water.

Silicon Hexethyl, or Hexethyl-silicoethane, $Si_2(C_2H_5)_6$, is formed by the action of zinc ethyl upon Si_2I_6 (obtained from I_4Si by means of silver). It is a liquid, boiling from 250–253°.

On heating ethyl silicate, $Si(O.C_2H_5)_4$ (p. 156), with zinc ethyl and sodium, the ethoxyl groups, $(O.C_2H_5)$, are successively replaced by ethyl groups. The product is a mixture of mono-, di- and triethylsilicon esters and silicon tetraethide, which are separated by fractional distillation.

Triethylsilicon Ethylate, $(C_2H_5)_3\overset{IV}{Si}.O.C_2H_5$, is a liquid, boiling at 153°, insoluble in water, and having a sp. gr. 0.841 at 0°. Acetyl oxide converts it into the acetic ester, which yields *triethylsilicon hydroxide*, $(C_2H_5)_3Si.OH$, when saponified with potash. The latter is sometimes called *triethylsilicol;* it is analogous to triethyl carbinol, $(C_2H_5)_3C.OH$, and deports itself like an alcohol. It is an oily liquid, insoluble in water.

Diethylsilicon-diethylate, $(C_2H_5)_2Si.(O.C_2H_5)_2$. An agreeable-smelling liquid, insoluble in water, and boiling at 155.8°. Its sp. gr. equals 0.875 at 0°. On treating it with acetyl chloride the compounds $(C_2H_5)_2Si\begin{matrix}\diagup O.C_2H_5\\ \diagdown Cl\end{matrix}$, and $(C_2H_5)_2SiCl_2$, are formed. The latter is a liquid, boiling at 148°. It fumes in air, and with water yields diethylsilicon oxide, $(C_2H_5)_2SiO$, analogous to diethyl ketone, $(C_2H_5)_2CO$.

Ethylsilicon-triethylate, $(C_2H_5)Si(O.C_2H_5)_3$, is a liquid with a camphor like odor, boiling at 159°, and slowly decomposed by water. Heated with acetyl chloride it forms ethyl silicon trichloride, $(C_2H_5)SiCl_3$. This liquid fumes strongly in the air, boils at about 100°, and when treated with water passes into ethyl silicic acid, $(C_2H_5)SiO.OH$ (Silico-propionic acid), which is analogous to propionic acid, $C_2H_5.CO.OH$, in constitution. It is a white, amorphous powder, that becomes incandescent when heated in the air. It dissolves in potassium and sodium hydroxides to form salts.

METALLO-ORGANIC COMPOUNDS.

The metallo-organic compounds are those resulting from the union of metals with monovalent alkyls; those with the bivalent alkylens have not yet been prepared. Inasmuch as we have no marked line of difference between metals and non-metals, the metallo-organic derivatives attach themselves, on the one side, by the derivatives of antimony and arsenic, to the phosphorus and nitrogen bases; and on the other, through the selenium compounds, to the sulphur alkyls and ethers. The tin derivatives approach the silicon alkyls and the hydrocarbons.

Upon examining the metals as they arrange themselves in the periodic system it is rather remarkable to find that it is only those which attach themselves to the electro-negative non-metals that are capable of yielding alkyl derivatives. In the three large periods this power manifests and extends itself only as far as the group of zinc (Zn, Cd, Hg). (Compare *Inorganic Chemistry.*) The alkyl derivatives of potassium and sodium, which cannot be isolated and are non-volatile, appear to possess a constitution analogous to that of the hydrogen compounds, Na_2H and K_2H, or sodium acetylene, C_2HNa.

Those compounds in which the metals present their maximum valence, *e.g.*,

$$\overset{II}{Hg}(CH_3)_2 \qquad \overset{III}{Al}(CH_3)_3 \qquad \overset{IV}{Sn}(CH_3)_4 \qquad \overset{IV}{Pb}(CH_3)_4 \qquad \overset{V}{Sb}(CH_3)_5,$$

are volatile liquids, usually distilling undecomposed in vapor form; therefore, the determination of their vapor density is an accurate means of establishing their molecular weight, and the valence of the metals. Being saturated compounds, they are incapable of taking up additional affinities.

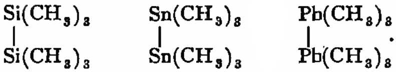
The behavior of the metallo-organic radicals, derived from the molecules by the separation of single alkyls, is especially noteworthy. The monovalent radicals, *e. g.*,

$$\overset{II}{Hg}(CH_3)— \quad \overset{III}{Tl}(CH_3)_2— \quad \overset{IV}{Sn}(CH_3)_3— \quad \overset{IV}{Pb}(CH_3)_3— \quad \overset{V}{Sb}(CH_3)_4—,$$

show great resemblance to the alkali metals in all their derivatives. Like other monovalent radicals they cannot be isolated. They yield hydroxides, *e. g.*,

$$Hg(C_2H_5).OH \qquad Tl(CH_3)_2.OH \qquad Sn(CH_3)_3.OH,$$

perfectly similar to KOH and NaOH. Some of the monovalent radicals, when separated from their compounds, double themselves (derivatives of metals of the silicon group):—



$$\begin{array}{c}Si(CH_3)_3\\ |\\ Si(CH_3)_3\end{array}\qquad\begin{array}{c}Sn(CH_3)_3\\ |\\ Sn(CH_3)_3\end{array}\qquad\begin{array}{c}Pb(CH_3)_3\\ |\\ Pb(CH_3)_3\end{array}.$$

By the exit of two alkyls from the saturated compounds, the bivalent radicals result:—

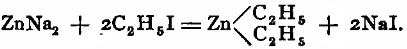
$$=\overset{III}{Bi}(CH_3)\qquad=\overset{IV}{Te}(CH_3)_2\qquad=\overset{IV}{Sn}(C_2H_5)_2\qquad=\overset{V}{Sb}(CH_3)_3.$$

In their compounds (oxides and salts) these resemble the bivalent alkaline earth metals, or the metals of the zinc group. A few of them occur in free condition. As unsaturated molecules, however, they are highly inclined to saturate two affinities directly. Antimony triethyl, $Sb(C_2H_5)_3$ (see p. 175), and apparently, too, tellurium diethyl, $Te(C_2H_5)_2$, have the power of uniting with acids to form salts; hydrogen is liberated at the same time. This would indicate a distinct metallic character.

Finally, the trivalent radicals, like $\overset{V}{As}(CH_3)_2$, can also figure as monovalent. This is the case, too, with vinyl, C_2H_3. These may be compared to aluminium, and the so-called cacodylic acid, $As(CH_3)_2O.OH$ (p. 173), to aluminium metahydrate, $AlO.OH$.

We conclude, therefore, that the electro-negative metals, by the successive union of alcohol radicals, always acquire a more strongly impressed basic, alkaline character. This also finds expression with the non-metals (sulphur, phosphorus, arsenic, etc.). (Compare pp. 145 and 170.) All the reactions of the alkyl compounds indicate that the various properties of the elementary atoms may be explained by the supposition of yet simpler primordial substances. (See Inorganic Chemistry.)

Most of the metallo-organic compounds can be prepared by the direct action of the metals, or their sodium amalgams, upon the bromides and iodides of the alkyls:—



$$ZnNa_2 + 2C_2H_5I = Zn\left\langle\begin{matrix}C_2H_5\\ C_2H_5\end{matrix}\right. + 2NaI.$$

Derivatives of the electro-negative metals can also be formed from the metallic chlorides by the action of zinc and mercury alkyls:—

$$SnCl_4 + 2Zn(CH_3)_2 = Sn(CH_3)_4 + 2ZnCl_2.$$

COMPOUNDS OF THE ALKALI METALS.

When sodium or potassium is added to zinc methide or ethide, zinc separates at the ordinary temperature, and from the solution that is thus produced, crystalline compounds deposit on cooling. The liquid retains a great deal of unaltered zinc alkyl, but it also appears to contain the sodium and potassium compounds—at least it sometimes reacts quite differently from the zinc alkyls. Thus, it absorbs carbon dioxide, forming salts of the fatty acids:—

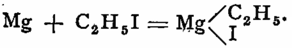
$$C_2H_5Na + CO_2 = \underset{\text{Sodium Propionate.}}{C_2H_5.CO_2Na.}$$

The ketones are produced by the action of carbon monoxide. These supposed alkali derivatives (p. 177) cannot be isolated, because when heat is applied to them, potassium and sodium separate and decomposition ensues. Their solutions are energetically oxidized when exposed to the air. Water decomposes them with extreme violence.

COMPOUNDS OF THE METALS OF THE MAGNESIUM GROUP.

1. **Beryllium Ethide**, $Be(C_2H_5)_2$, is formed by heating beryllium with mercury ethyl. It is a colorless liquid, boiling from 185°–188°. It fumes strongly in the air and ignites spontaneously. Water decomposes it with violence, beryllium hydroxide, $Be(OH)_2$, separating. **Beryllium Propyl**, $Be(C_3H_7)_2$, boils about 245°.

2. **Magnesium Ethide**, $Mg(C_2H_5)_2$. On warming magnesium filings with ethyl iodide away from contact with the air, magnesium ethyl iodide first results :—



$$Mg + C_2H_5I = Mg\Big\langle\begin{matrix}C_2H_5\\ I\end{matrix}.$$

on applying heat to this it decomposes according to the following equation :—

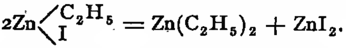
$$2Mg(C_2H_5)I = Mg(C_2H_5)_2 + MgI_2.$$

Magnesium ethide is a liquid that takes fire on exposure to the air, and is decomposed by water with the production of ethane :—

$$Mg(C_2H_5)_2 + H_2O = 2C_2H_6 + MgO.$$

3. *Zinc compounds.*

The reaction observed above with magnesium may occur here, *i. e.*, when zinc filings act upon iodides of the alcohol radicals in sunlight, iodides are formed, which are decomposed by heat :—



$$2Zn\Big\langle\begin{matrix}C_2H_5\\ I\end{matrix} = Zn(C_2H_5)_2 + ZnI_2.$$

The dialkyl derivatives may be obtained by heating a solution of the alkyl iodides, in absolute ether, with granulated zinc or zinc turnings, in closed vessels, to 100°–200° (Frankland).

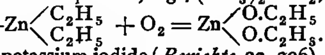
The reaction occurs at a lower temperature if an alloy of zinc and sodium be employed as a substitute for the metallic zinc. The operation is as follows: in a flask provided with a doubly perforated caoutchouc cork, bearing an inverted condenser, there is introduced a mixture of the alkyl iodide with ether and zinc-sodium. The air is expelled from the vessel by a current of carbon dioxide, and the heat of a water bath is then applied to it. When the reaction is complete, the condenser is reversed, and the zinc compound distilled off in a current of CO_2.

Pure zinc turnings may replace the zinc-sodium if they have been previously attacked by sulphuric acid, and the pressure of the apparatus increased. This may be accomplished by connecting the inner tube of the condenser with another tube extending into mercury. The most convenient method of preparing zinc ethide is to let ethyl iodide act upon zinc-copper. (*Berichte*, 6, 200.)

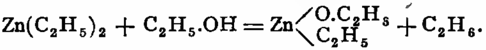
The zinc alkyls are colorless liquids, fuming strongly in the air and igniting readily; therefore, they can only be handled in an atmosphere of carbon dioxide. They inflict painful wounds when brought in contact with the skin. Water decomposes them very energetically, forming hydrocarbons and zinc hydroxide:—

$$Zn(CH_3)_2 + 2H_2O = 2CH_4 + Zn(OH)_2.$$

Oxygen is added by slow oxidation in the air and compounds, *e. g.*, $(CH_3)_2ZnO_2$, analogous to peroxides, are produced:—$Zn\begin{smallmatrix}/C_2H_5\\ \backslash C_2H_5\end{smallmatrix} + O_2 = Zn\begin{smallmatrix}/O.C_2H_5\\ \backslash O.C_2H_5\end{smallmatrix}$. These explode readily and liberate iodine from potassium iodide (*Berichte*, 23, 396).



The alcohols convert the zinc alkyls into zinc alcoholates and hydrocarbons:—



$$Zn(C_2H_5)_2 + C_2H_5.OH = Zn\begin{smallmatrix}/O.C_2H_5\\ \backslash C_2H_5\end{smallmatrix} + C_2H_6.$$

The free halogens decompose both the zinc alkyls and those of other metals very energetically:—

$$Zn(C_2H_5)_2 + 2Br_2 = 2C_2H_5Br + ZnBr_2.$$

Zinc Methide, $Zn(CH_3)_2$, is a disagreeably smelling, mobile liquid, which boils at 46°. Its sp. gr. at 10° is 1.386.

Zinc Ethide, $Zn(C_2H_5)_2$, boils at 118°, and has the sp. gr. 1.182 at 18°. With alcohol it yields zinc alcoholate and ethane:—

$$Zn(C_2H_6)_2 + 2C_2H_5.OH = Zn(O.C_2H_5)_2 + 2C_2H_6.$$

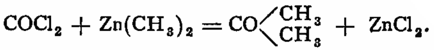
Sulphur dissolves in it, forming zinc mercaptide, $Zn(S.C_2H_6)_2$.

Zinc Isoamyl, $Zn(C_5H_{11})_2$, boils at 220°, fumes strongly in the air, but does not ignite spontaneously.

The zinc alkyls are very reactive, hence, serve for the preparation of many other compounds. Thus, they readily react with chlorides of the heavy metals and the metalloids, whereby alkyl derivatives of the latter are produced (p. 178). The hydrocarbons (see p. 71) are produced when they are heated to 150° with alkyl iodides:—

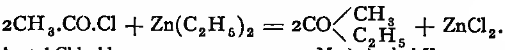
$$Zn(C_2H_5)_2 + 2C_3H_5I = \underset{\text{Ethyl-allyl.}}{2C_2H_5.C_3H_5} + ZnI_2.$$

Carbon oxychloride converts them into ketones:—



$$COCl_2 + Zn(CH_3)_2 = CO\begin{smallmatrix}/CH_3\\ \backslash CH_3\end{smallmatrix} + ZnCl_2.$$

The ketones are also produced in the action of the zinc alkyls upon the chlorides of the acid radicals in the cold:—



$$\underset{\text{Acetyl Chloride.}}{2CH_3.CO.Cl} + Zn(C_2H_6)_2 = \underset{\text{Methyl-ethyl Ketone.}}{2CO\begin{smallmatrix}/CH_3\\ \backslash C_2H_5\end{smallmatrix}} + ZnCl_2.$$

Acetyl Chloride. Methyl-ethyl Ketone.

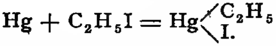
When an excess of the zinc alkyl is employed, tertiary alcohols are formed (p. 120).

The zinc alkyls unite with the aldehydes and ketones to form compounds, which are decomposed by water into higher secondary and tertiary alcohols (p. 120). The alkyl oxides and the alkylen oxides are not affected by the zinc alkyls (*Berichte*, 17, 1968).

The zinc alkyls absorb sulphur dioxide and become zinc salts of the sulphinic acids (p. 154). Nitric oxide dissolves in zinc diethyl and forms a crystalline compound, from which the zinc salts of the so-called dinitroethylic acid, $C_2H_5.N_2O_2H$, is obtained by the action of water and CO_2.

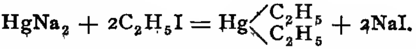
4. *Mercury Compounds.*

These are formed according to methods similar to those employed for the zinc compounds. The alkyl iodides unite with mercury at ordinary temperatures to yield iodides (sunlight is favorable):—



$$Hg + C_2H_5I = Hg\left\langle\begin{matrix}C_2H_5\\I.\end{matrix}\right.$$

The dialkyl compounds are produced when sodium amalgam acts upon the alkyl iodides:—



$$HgNa_2 + 2C_2H_5I = Hg\left\langle\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right. + 2NaI.$$

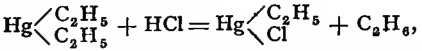
The reaction may be executed as follows: Liquid sodium amalgam is gradually added to the mixture of the iodide or bromide with $\frac{1}{10}$ volume ethyl acetate, accompanied by frequent shaking of the vessel; the reaction occurs then with increase of heat. When the mass becomes syrupy, it is distilled, and the operation repeated until all the iodide is decomposed (until on boiling with HNO_3, iodine no longer separates). The oily distillate is shaken with potassium hydroxide to decompose the ethyl acetate, the heavy oily mercury alkyl separated, and after drying with calcium chloride it is distilled. (*Annalen*, 103, 105 and 109.)

The action of zinc alkyls upon mercuric chloride also produces them:—

$$HgCl_2 + (C_2H_5)_2Zn = Hg(C_2H_5)_2 + ZnCl_2.$$

These compounds are colorless, heavy liquids, possessing a faint, peculiar odor. Their vapors are extremely poisonous. Water and air occasion no change in them, but when heated they ignite easily.

The haloid acids cause one alkyl group to split off, leaving salts of the monoalkyl derivatives:—



$$Hg\left\langle\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right. + HCl = Hg\left\langle\begin{matrix}C_2H_5\\Cl\end{matrix}\right. + C_2H_6,$$

and when moist silver oxide acts on the halogen derivatives, *hydroxyl* compounds are produced:—

$$Hg(C_2H_5)Cl + AgOH = Hg(C_2H_5).OH + AgCl;$$

these are strongly alkaline, and form crystalline salts with the acids.

One and two alkyls separate from the mercury alkyls by the action of the halogens:—

$$\begin{aligned} Hg(C_2H_5)_2 + I_2 &= Hg(C_2H_5)I + C_2H_5I \text{ and} \\ Hg(C_2H_5)I + I_2 &= HgI_2 \qquad\quad + C_2H_5I. \end{aligned}$$

Mercury-Methyl, $Hg(CH_3)_2$, is a liquid having a specific gravity of 3.069; it boils at 95°, and is but slightly soluble in water. When a molecule of iodine is added to its alcoholic solution there is formed mercury methyl iodide, $Hg(CH_3)I$, insoluble in water, but soluble in alcohol, from which it crystallizes in shining leaflets, fusing at 143°. Potassium cyanide converts the iodide again into mercury-methyl. When treated with silver nitrate the salt, $Hg(CH_3).O.NO_2$, is produced.

Mercury Ethide, $Hg(C_2H_5)_2$, has a specific gravity of 2.44, and boils at 159°. At 200° it decomposes into Hg and C_4H_{10}. Its *chloride*, $Hg(C_2H_5)Cl$, separates in brilliant needles, when its alcoholic solution is digested with $HgCl_2$. Direct sunlight decomposes the *iodide* into Hg and C_4H_{10}. These halogen derivatives when treated with moist silver oxide, yield *mercury ethyl hydroxide*, $Hg(C_2H_5).OH$, a thick liquid of strong alkaline reaction, and soluble in both water and alcohol. It forms crystalline salts with the acids.

Mercury-Allyl Iodide, $Hg(C_3H_5)I$, is obtained when allyl iodide is shaken with mercury. It crystallizes from alcohol in shining leaflets, fusing at 135°. Propylene results when hydriodic acid acts on the iodide:—

$$Hg(C_3H_5)I + HI = HgI_2 + C_3H_6.$$

COMPOUNDS OF THE METALS OF THE ALUMINIUM GROUP.

The aluminium alkyl derivatives attach themselves to those springing from boron (p. 175); however, it appears that only those exist in which three alkyls are present. They are produced by the action of the mercury alkyls upon aluminium filings:—

$$2Al + 3Hg(CH_3)_2 = 2Al(CH_3)_3 + 3Hg.$$

Aluminium-Methyl, $Al(CH_3)_3$, boils at 130°, and crystallizes at 0°. It fumes in the air, and is spontaneously inflammable. Water decomposes it with great violence, forming ethane and aluminium hydroxide. Its vapor density has been found to be 2.8 (or 35.6, $H = 1$) at 240°; this would answer to the molecular formula $Al(CH_3)_3 = 72.3$. It, however, appears that at low temperatures the molecules $Al_2(CH_3)_6$ also exist (see *Berichte*, 22, 551).

Aluminium-Ethyl, $Al(C_2H_5)_3$, is perfectly analogous to the preceding compound, but does not solidify in the cold. It boils at 194°. At 240° its vapor density has been found equal to 4.5 (or 64, $H = 1$), almost corresponding to the molecular formula $Al(C_2H_5)_3 = 114.3$.

The derivatives of trivalent gallium and indium have not been prepared.

The thallium-diethyl compounds, $Tl(C_2H_5)_2X$, are known.

Thallium-Diethyl Chloride, $Tl(C_2H_5)_2Cl$, is formed when zinc ethide is allowed to act upon thallium chloride:—

$$TlCl_3 + Zn(C_2H_5)_2 = Tl(C_2H_5)_2Cl + ZnCl_2.$$

Thallium-diethyl salts, *e.g.*, $Tl(C_2H_5)_2O.NO_2$, are obtained from this by double decomposition with silver salts. If the sulphate be decomposed with barium hydrate, *thallium-diethyl hydroxide*, $Tl(C_2H_5)_2.OH$, is obtained. This is readily soluble in water, crystallizes therefrom in glistening needles, and has a strong alkaline reaction.

COMPOUNDS OF THE METALS OF THE GERMANIUM GROUP.

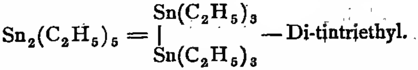
The alkyl derivatives of the tetravalent metals, germanium (72.3), tin (117) and lead (206), are perfectly analogous in constitution to those of silicon (p. 176) belonging to the same group; the differences in reaction of the tin and lead compounds are induced by the more positive, metallic nature of tin and lead (see p. 178). The compounds of germanium form the transition to those of silicon and tin.

1. **Germanium-Ethide,** $Ge(C_2H_5)_4$, is formed when zinc ethide acts upon germanium chloride. It is a liquid with a leek-like odor. It boils at 160°, and its sp. gr. is 0.96. At ordinary temperatures it is not altered on exposure to the air.

2. **Tin Compounds.**—In addition to the saturated derivatives with four alkyls, *tin* is also capable of uniting with three and two alkyls to groups which act like *basic radicals*, forming salt-like compounds with negative groups:—

$Sn(C_2H_5)_4$	Tin tetraethyl
$Sn(C_2H_5)_3Cl$	Tin triethyl chloride
$Sn(C_2H_5)_2Cl_2$	Tin diethyl chloride.

Tin diethyl, $Sn(C_2H_5)_2$, appears to exist as an unsaturated molecule (like tin dichloride, $SnCl_2$), while the group, $Sn(C_2H_5)_3$, in free condition doubles itself:—



$$Sn_2(C_2H_5)_6 = \begin{array}{l} Sn(C_2H_5)_3 \\ | \\ Sn(C_2H_5)_3 \end{array} \text{—Di-tintriethyl.}$$

Tin Tetraethyl, Stannic Ethide, $Sn(C_2H_5)_4$, is best prepared by distilling tin chloride with zinc ethyl;—

$$SnCl_4 + 2Zn(C_2H_5)_2 = Sn(C_2H_5)_4 + 2ZnCl_2.$$

It is a colorless, ethereal smelling liquid, boiling at 181° and possessing a specific gravity of 1.187 at 23°. Its vapor density equals 8.02 or 116 (H = 1). It is insoluble in water and does not suffer change on exposure to the air. By the action of the halogens the alkyls are successively eliminated;—

$$\begin{aligned} Sn(C_2H_5)_4 + I_2 &= Sn(C_2H_5)_3I + C_2H_5I \\ Sn(C_2H_5)_3I + I_2 &= Sn(C_2H_5)_2I_2 + C_2H_5I \\ Sn(C_2H_5)_2I_2 + I_2 &= SnI_4 + 2C_2H_5I. \end{aligned}$$

Hydrochloric acid acts similarly:—

$$Sn(C_2H_5)_4 + HCl = Sn(C_2H_5)_3Cl + 2C_2H_3, \text{ etc.}$$

Tin Tetramethyl, $Sn(CH_3)_4$, is similar to the preceding, boils at 78°, and has a specific gravity at 0° of 1.314.

On heating an alloy of tin and a little sodium (about 2 per cent.) with ethyl iodide, there results a mixture consisting of $Sn(C_2H_5)_3I$ and $Sn(C_2H_5)_2I_2$, which may be separated by fractionation. With an alloy rich in sodium (about 20 per cent.) the products are $Sn(C_2H_5)_2$ and $Sn_2(C_2H_5)_6$; the latter is almost insoluble in alcohol, while the first is very soluble and can be re-precipitated by water.

Tin-Triethyl Iodide, $Sn(C_2H_5)_3I$, is a colorless oil, insoluble in water and having a disagreeable smell. It boils at 231°, and has a specific gravity of 1.833 at 22°. Hydrochloric acid precipitates the *chloride*, $Sn(C_2H_5)_3Cl$, from tin triethyl salts, as a heavy oil, which solidifies at 0°. It boils from 208–210°, and has a specific gravity of 1.428. Alcohol is a solvent for both. When either one is acted upon by silver oxide or caustic potash, there is produced:—

Tin-Triethyl Hydroxide, $Sn(C_2H_5)_3.OH$, crystallizing in shining prisms, melting at 66°, and boiling undecomposed at 272°. It volatilizes along with the steam. It is sparingly soluble in water, but dissolves readily in alcohol and ether. It reacts strongly alkaline, absorbs carbon dioxide, and yields crystalline salts with the acids, *e. g.*, $Sn(C_2H_5)_3.O.NO_2$. When the hydroxide is heated for some time to almost the boiling temperature, it breaks up into water and *tin-triethyl oxide*, $\begin{array}{l}Sn(C_2H_5)_3\\Sn(C_2H_5)_3\end{array}\!\!>O$, an oily liquid, which in the presence of water at once regenerates the hydrate.

Free Tin-Triethyl, $\begin{array}{l}Sn(C_2H_5)_3\\|\\Sn(C_2H_5)_3\end{array} = Sn_2(C_2H_5)_6$, or *Stannoso-stannic Ethide*, is produced, as already described, by heating tin-sodium with ethyl iodide; also on warming tin-triethyl iodide with sodium:—

$$2Sn(C_2H_5)_3I + Na_2 = Sn_2(C_2H_5)_6 + 2NaI.$$

It is a liquid, of mustard-like odor, insoluble in alcohol, but readily soluble in ether. It distils with slight decomposition at 265–270°. It combines with oxygen, forming tin-triethyl oxide, $\begin{array}{l}Sn(C_2H_5)_3\\Sn(C_2H_5)_3\end{array}\!\!>O$, and with iodine yields tin-triethyl iodide:—

$$\begin{array}{l}Sn(C_2H_5)_3\\|\\Sn(C_2H_5)_3\end{array} + I_2 = 2Sn(C_2H_5)_3I.$$

Tin-Diethyl, or Stannous Ethide, $Sn(C_2H_5)_2$. Its preparation is described above. It is a thick oil, decomposed when distilled, therefore its molecular weight has not been determined. It combines with oxygen and the halogens:—

$$Sn(C_2H_5)_2 + I_2 = Sn(C_2H_5)_2I_2.$$

When distilled it decomposes completely into tin and tin-tetraethyl:—

$$2Sn(C_2H_5)_2 = Sn(C_2H_5)_4 + Sn.$$

Tin-Diethyl Chloride, $Sn(C_2H_5)_2Cl_2$, is best prepared by dissolving tin-diethyl-oxide in hydrochloric acid. It is insoluble in water, alcohol and ether, crystallizes in needles, fusing at 60° and boils at 220°. The *iodide*, $Sn(C_2H_5)_2I_2$, is also produced by the action of ethyl iodide in sunlight upon zinc filings. It crystallizes in needles, fuses at 44.5°, and boils at 245°.

Ammonium hydroxide and the alkalies precipitate from aqueous solutions of both the halogen compounds:—

Tin-Diethyl Oxide, $Sn(C_2H_5)_2O$, a white, insoluble powder. It is soluble in excess of alkali, and forms crystalline salts with the acids, *e. g.*, $Sn(C_2H_5)_2\langle{}^{O.NO_2}_{O.NO_2}$.

3. LEAD COMPOUNDS.

These are very similar to the preceding; derivatives with two alkyls do not, however, exist:—

$Pb(C_2H_5)_4$	Lead tetraethyl.
$Pb(C_2H_5)_3Cl$	Lead triethyl chloride.
$Pb_2(C_2H_5)_6$	Di-leadtriethyl.

Lead-Tetraethyl, $Pb(C_2H_5)_4$, is obtained by heating lead chloride with zinc ethide:—

$$2PbCl_2 + 2Zn(C_2H_5)_2 = Pb(C_2H_5)_4 + 2ZnCl_2 + Pb.$$

It is an oily liquid, distilling out of air contact at about 200°, with partial decomposition. When heated in the air it takes fire and burns with an orange-colored flame. When hydrogen chloride acts upon it, ethane is evolved and *Lead Triethyl chloride*, $Pb(C_2H_5)_3Cl$, formed, which crystallizes in silky, shining needles. The *iodide*, $Pb(C_2H_5)_3I$, is very similar to the last, and is produced when iodine acts upon lead-tetraethyl. On heating either of these derivatives with silver oxide or caustic potash, *lead-triethyl hydroxide*, $Pb(C_2H_5)_3.OH$, distils over. This reacts very alkaline, and forms crystalline salts with the acids. The sulphate, $[Pb(C_2H_5)_3]_2SO_4$, dissolves in water with difficulty.

Lead-Triethyl, $Pb_2(C_2H_5)_6$, is obtained by the action of ethyl iodide on an alloy of lead and sodium:—

$$2PbNa_3 + 6C_2H_5I = Pb_2(C_2H_5)_6 + 6NaI.$$

Lead triethyl is a yellowish liquid, insoluble in water, possessing a sp. gr. of 1.471 at 10°, and boiling with partial decomposition. It reacts energetically with the halogens:—

$$Pb_2(C_2H_5)_6 + I_2 = 2Pb(C_2H_5)_3I.$$

The lead-methyl derivatives are perfectly analogous to the ethyl compounds.

Consult *Berichte*, 22, 467, for the experiments made with the view of preparing *Titanium-Tetraethyl*, $Ti(C_2H_5)_4$.

COMPOUNDS OF BISMUTH.

These arrange themselves with those derived from antimony and arsenic; but in accordance with the complete metallic nature of bismuth, we do not meet any compounds here analogous to stibonium (p. 171) or arsonium.

Bismuth-Trimethyl, $Bi(CH_3)_3$, results from the interaction of zinc ethide and bismuth tribromide. It is a mobile, strongly refracting liquid, with a disagreeable odor. Its sp. gr. is 2.3 at 18°. It fumes in the air, and oxidizes rapidly. It explodes if heated in air. Surrounded by an indifferent gas it boils at 110° without decomposition (*Berichte*, 20, 1516; 21, 2035).

Bismuth-Triethyl, $Bi(C_2H_5)_3$, is formed by acting upon an alloy of bismuth and potassium with ethyl iodide. It is perfectly similar to the methide, and inflames rapidly on exposure to the air. It explodes if heated to 150°. It distils without decomposition under reduced pressure (below 7.9 mm. at 107°). It reacts very energetically with the halogens, according to the equation:—

$$Bi(C_2H_5)_3 + 2I_2 = Bi(C_2H_5)I_2 + 2C_2H_5I.$$

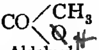
Bismuth-ethyl Chloride, $Bi(C_2H_5)Cl_2$, is formed when mercuric chloride acts on bismuth-triethyl:—

$$Bi(C_2H_5)_3 + 2HgCl_2 = Bi(C_2H_5)Cl_2 + 2Hg(C_2H_5)Cl.$$

The *iodide,* $Bi(C_2H_5)I_2$, results when the chloride is warmed with KI. This salt crystallizes in yellow leaflets. From its alcoholic solution the alkalies precipitate *Bismuth-ethyl oxide,* $Bi(C_2H_5)O$, an amorphous, yellow powder, which takes fire readily in the air. The *nitrate,* $Bi(C_2H_5)\begin{matrix}\diagup O.NO_2\\ \diagdown O.NO_2\end{matrix}$, is produced by adding silver nitrate to the iodide. This crystallizes from alcohol, explodes on being warmed, and is decomposed by water with formation of bismuth dinitrate, $Bi(OH)(NO_3)_2$.

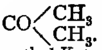
ALDEHYDES AND KETONES.

Aldehydes and ketones contain the carbonyl group CO, which in the latter unites two alkyls, but in the former is combined with only one alkyl and one hydrogen atom:—



$$CO\begin{matrix}\diagup CH_3\\ \diagdown \cancel{Q}\ H\end{matrix}$$

Aldehyde.



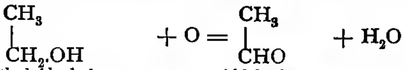
$$CO\begin{matrix}\diagup CH_3\\ \diagdown CH_3.\end{matrix}$$

Dimethyl Ketone.

This expresses the similarity and the difference in character of aldehydes and ketones.

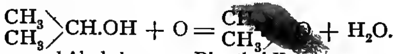
The methods of preparation common to both classes of compounds are:—

1. Oxidation of the alcohols, whereby the primary alcohols change to aldehydes and the secondary to ketones (see p. 118):—



$$\begin{matrix}CH_3\\ |\\ CH_2.OH\end{matrix} + O = \begin{matrix}CH_3\\ |\\ CHO\end{matrix} + H_2O$$

Ethyl Alcohol. Aldehyde.



$$\begin{matrix}CH_3\diagdown\\ CH_3\diagup\end{matrix}CH.OH + O = \begin{matrix}CH_3\diagdown\\ CH_3\diagup\end{matrix}CO + H_2O.$$

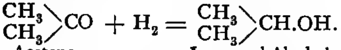
Isopropyl Alcohol. Dimethyl Ketone.

The above oxidation may be effected by oxygen; or air in presence of platinum sponge, or by ozone. It takes place more readily on warming the alcohols with potassium dichromate (or MnO_2) and dilute sulphuric acid. To prevent the oxidation extending too far, it is sometimes recommended to employ an aqueous solution of chromic acid (*Berichte*, 5, 699).

Conversely, aldehydes and ketones again become primary and secondary alcohols by an addition of hydrogen :—

$$CH_3.CHO + H_2 = CH_3.CH_2.OH$$

Aldehyde. Ethyl Alcohol.



$$\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right\rangle CO + H_2 = \left.\begin{matrix}CH_3\\CH_3\end{matrix}\right\rangle CH.OH.$$

Acetone. Isopropyl Alcohol.

Further oxidation converts the aldehydes into acids, but the ketones suffer decomposition by means of it :—

$$CH_3.CHO + O = CH_3.CO.OH.$$

Aldehyde. Acetic Acid.

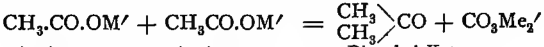
Empirically, the aldehydes are distinguished from the alcohols by possessing two atoms less of hydrogen—hence their name (from *Alkohol dehydrogenatus*), *e. g.*, ethyl aldehyde, propyl aldehyde, etc., etc. On account of their intimate relationship to the acids, their names are also derived from the latter, like acetaldehyde, propionic aldehyde, etc.

2. The dry distillation of a mixture of the calcium, or better, barium salts of two monobasic fatty acids. Should in this case one of the acids be formic acid, aldehydes are produced :—

$$CH_3.CO.OM' + HCO.OM' = CH_3.COH + CO_3Me'_2$$

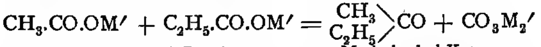
An Acetate. Formate. Acetaldehyde.

In all other instances ketones result, and they are either *simple*, with two similar alkyls, or *mixed*, with two dissimilar alkyls :—



$$CH_3.CO.OM' + CH_3CO.OM' = \left.\begin{matrix}CH_3\\CH_3\end{matrix}\right\rangle CO + CO_3Me_2'$$

An Acetate. An Acetate. Dimethyl Ketone.



$$CH_3.CO.OM' + C_2H_5.CO.OM' = \left.\begin{matrix}CH_3\\C_2H_5\end{matrix}\right\rangle CO + CO_3M_2'$$

An Acetate. A Propionate. Methyl-ethyl Ketone.

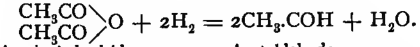
When working with higher aldehydes, which volatilize with difficulty, and ketones, it is advisable to distil in vacuo.

Both aldehydes and ketones combine with primary alkaline sulphites, yielding crystalline compounds (see later).

ALDEHYDES.

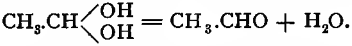
The aldehydes, *e. g.*, acetaldehyde, $CH_3.CHO$, are compounds containing the group COH, which is readily formed by the oxidation of the primary alcoholic group, $CH_2.OH$ (p. 117). Again, in accordance with their fatty acid origin, aldehydes may be viewed as the hydrogen derivatives of the *acid radicals*. This would explain their formation by the action of nascent hydrogen (sodium amalgam) upon the chlorides of acid radicals, or their oxides (the acid anhydrides):—

$$\underset{\text{Acetyl Chloride.}}{CH_3.COCl} + H_2 = \underset{\text{Acetaldehyde.}}{CH_3.COH} + HCl,$$



$$\underset{\text{Acetic Anhydride.}}{\left.\begin{matrix}CH_3CO\\CH_3CO\end{matrix}\right>O} + 2H_2 = \underset{\text{Acetaldehyde.}}{2CH_3.COH} + H_2O.$$

Hence, they may be regarded as the oxides of bivalent radicals (like $CH_3.CH =$ ethidene), or as the anhydrides of the very unstable dihydroxyl derivatives of these. Wherever the formation of these latter compounds occurs we can expect, from their close analogy to the glycols, that water will split off and the aldehydes result:—



$$CH_3.CH\left<\begin{matrix}OH\\OH\end{matrix}\right. = CH_3.CHO + H_2O.$$

This explains the formation of *e.g.*, acetaldehyde (ethidene oxide) from ethidene chloride, CH_3CHCl_2, when heated with water (more readily in presence of lead oxide), and also its production from the ethereal and ester-like compounds, such as ethidene diacetate, $CH_3.CH(O.C_2H_3O)_2$, by saponification with alkalies or sulphuric acid. In a similar manner, on heating glycollic and lactic acids, $CH_2\left<\begin{matrix}OH\\CO_2H\end{matrix}\right.$, $CH_3.CH\left<\begin{matrix}OH\\CO_2H\end{matrix}\right.$, with acids, there occurs a splitting-off of formic acid (or of CO and H_2O) and the products are methylene oxide, CH_2O (formic aldehyde), acetaldehyde, $CH_3.CHO$, etc.

Besides these general methods the aldehydes, as the transitional members to the acids, frequently appear in the oxidation (by means of manganese peroxide and dilute sulphuric acid, or a chromic acid solution) of complex substances such as the albuminoids.

The aldehydes exhibit in their properties a gradation similar to that of the alcohols. The lower members are volatile liquids, soluble in water, and have a peculiar odor, but the higher are solids, insoluble in water, and cannot be distilled without decomposition. In general they are more volatile and dissolve with more difficulty in water than the alcohols. In chemical respects the aldehydes are neutral substances, yet they are easily oxidized to acids on exposure to the air:—

$$CH_3.CHO + O = CH_3.CO.OH.$$

Their ready oxidation by the oxides and salts of the noble metals (the latter being separated in free condition) is characteristic of aldehydes. On adding an aqueous aldehyde solution to a weak ammoniacal silver nitrate solution, silver separates on the sides of the vessel as a brilliant mirror.

The reaction is more delicate in the presence of caustic potash (*Berichte*, 15, 1635 and 1828); such a solution will even reduce cane sugar and glycerol when assisted by heat. Alkaline copper solutions are reduced, too, by many fatty aldehydes (*Berichte*, 14, 675 and 1950). The reduction of alkaline silver and copper solutions is, however, not peculiar to the aldehyde groups alone, but belongs also to some other atomic groups (see acetone alcohol, glycid alcohol, hydrazine). A very delicate reaction of the aldehydes is their power of imparting an intense violet color to a fuchsine solution previously decolorized by sulphurous acid (*Berichte*, 14, 1848). Chloral hydrate and the glucoses do not, but some ketones do, show this reaction (*Berichte*, 14, 791). The following is more sensitive: Add an aldehyde and a little sodium amalgam to the sodium hydroxide solution of diazobenzene sulphonic acid and a violet-red coloration is produced. Grape sugar and other sugars, but not chloral, will do the same. Acetone and acetic ether produce a dark red coloration (*Berichte*, 16, 657, and 17, Ref. 385).

When oxygen or air is conducted through the hot solution of an aldehyde (like paraldehyde) in alcoholic potash, an intense light-display is observed; many aldehyde derivatives, and even grape sugar, deport themselves similarly (*Berichte*, 10, 321).

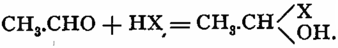
Nearly all the aldehydes are converted into resin by the alkalies; some are transformed into acids and alcohols by alcoholic alkali solutions:—

$$\underset{\text{Amyl Aldehyde.}}{2C_4H_9.COH} + KOH = \underset{\text{Pot. Valerate.}}{C_4H_9.CO.OK} + \underset{\text{Amyl Alcohol.}}{C_4H_9.CH_2.OH.}$$

Phosphorus pentachloride replaces the oxygen of aldehyde by two chlorine atoms (p. 92):—

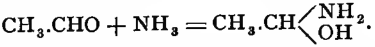
$$CH_3.CHO + PCl_5 = CH_3.CHCl_2 + PCl_3O.$$

Notwithstanding they are really saturated compounds, aldehydes possess, in a remarkable degree, the property of uniting two affinities directly, and thereby changing the oxygen united with two affinities to the hydroxyl group:—



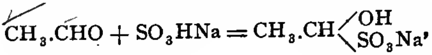
$$CH_3.CHO + HX = CH_3.CH\begin{cases}X\\OH.\end{cases}$$

Thus they become alcohols by the addition of two hydrogen atoms. They unite directly with ammonia to form crystalline compounds, called *aldehyde-ammonias*:—



$$CH_3.CHO + NH_3 = CH_3.CH\begin{cases}NH_2.\\OH\end{cases}$$

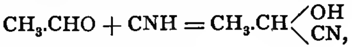
These are readily soluble in water but not in ether, hence ammonia gas will precipitate them in crystalline form from the ethereal solution of the aldehydes. They are rather unstable and dilute acids again resolve them into their components. Aldehydes unite in a similar manner with acid alkaline sulphites, forming crystalline compounds:—



$$CH_3.CHO + SO_3HNa = CH_3.CH\begin{cases}OH\\SO_3Na,\end{cases}$$

which may be regarded as salts of *oxysulphonic acids*. The aldehydes may be released from these salts by distillation with dilute sulphuric acid or soda. This procedure permits of the separation and purification of aldehydes from other substances.

Aldehydes also combine with hydrogen cyanide, yielding *oxycyanides* or cyanhydrins:—



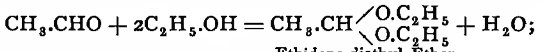
$$CH_3.CHO + CNH = CH_3.CH\Big\langle\begin{array}{l}OH\\CN,\end{array}$$

from which oxyacids are prepared.

These cyanides are often crystalline and may be prepared by prolonged heating of the aldehydes with a concentrated CNH solution, or by adding hydrochloric acid to a mixture of the aldehyde and pulverized potassium cyanide (*Berichte*, 14, 235 and 1965). When these compounds are distilled they usually break up into their components. The alkalies also cause a separation of CNH. When hydrochloric or sulphuric acid acts upon them they pass into oxyacids.

With ammonium cyanide aldehydes form *amidocyanides*, like $CH_3.CH\Big\langle\begin{array}{l}NH_2\\CN\end{array}$, which yield amido-acids (see these).

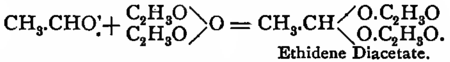
Being the oxides of the radicals, R.CH= (p. 188), aldehydes can, by direct additions, form ether and ester derivatives. Thus they combine at 100° with the alcohols and build the so-called *acetals*:—



$$CH_3.CHO + 2C_2H_5.OH = CH_3.CH\Big\langle\begin{array}{l}O.C_2H_5\\O.C_2H_5\end{array} + H_2O;$$

Ethidene-diethyl Ether.

and with the acid anhydrides they yield esters:—



$$CH_3.CHO + \begin{array}{l}C_2H_3O\\C_2H_3O\end{array}\Big\rangle O = CH_3.CH\Big\langle\begin{array}{l}O.C_2H_3O\\O.C_2H_3O.\end{array}$$

Ethidene Diacetate.

These compounds will be treated with the derivatives of the bivalent radicals.

The *polymerization* of the aldehydes depends upon a similar partial separation of the oxygen atoms and the union through the latter of several aldehyde radicals, $CH_3.CH=$. This occurs especially with the lower members of the series. Thus from formic aldehyde, CH_2O, arises trioxymethylene, $(CH_2O)_3$, from acetaldehyde, C_2H_4O, paraldehyde, $(C_2H_4O)_3$, and metaldehyde, $(C_2H_4O)_n$ (see p. 194).

The readiness with which the polymerides break up into simple molecules shows that in them the carbon atoms are not in union with each other; their power of refracting light (p. 60) would also indicate this (*Annalen*, 203, 44).

Finally, the aldehydes *condense* readily, *i. e.*, two molecules unite by means of two carbon atoms, and water may or may not separate (aldehyde and aldol condensation see p. 194).

By such an exit of water the aldehydes (also the ketones) are endowed with the power of entering into combination with free hydroxylamine (or its HCl-salt), and forming the so-called **aldoximes** (acetoximes) (V. Meyer):—

$$\underset{\text{Acetaldehyde.}}{CH_3.CHO} + H_2N.OH = \underset{\text{Ethyl Aldoxime.}}{CH_3.CH:N.OH} + H_2O.$$

These contain the bivalent *oximide* group, N.OH, combined with one carbon atom. They are isomerides of the nitroso-compounds (see p. 106), hence also designated the *isonitroso-derivatives* of the hydrocarbons. The aldoximes are, as a usual thing, liquid bodies that boil without decomposition. Ethers are produced when the hydrogen of their hydroxyl group is replaced by acid radicals, or by the alkali metals (by means of sodium alcoholate) and the alkyls. When boiled with acids they are again changed to aldehyde and hydroxylamine. By the action of acetic anhydride or acetyl chloride the aldoximes become nitriles, while the acetoximes are changed to acetyl esters (*Berichte*, 19, 1613, and 20, 501, 2196). Nascent hydrogen converts them into amines (p. 160).

The aldoximes result from all compounds which, like the aldehydes, contain the aldehyde group, CHO, *e. g.*, the aldehyde acids (*Berichte*, 15, 2783, 16, 823, and 1780). Paraldehyde and metaldehyde (see above) do not react with hydroxylamine. All the ketones and compounds containing the group CO, peculiar to them, yield corresponding *acetoximes* (see Ketones). These oximido- or isonitroso-derivatives do not show the nitroso reaction (see p. 164).

All the aldehydes (and the ketones) react more readily with phenyl hydrazine (*Berichte*, 16, 661, 17, 574) than with hydroxylamine to form oily or solid condensation products—the *hydrazones*:—

$$CH_3.CHO + H_3N_2.C_6H_5 = CH_3.CH:HN_2.C_6H_5 + H_2O.$$

These serve for the characterization and recognition of the aldehydes. Boiling acids break up the hydrazones into their components. Sodium amalgam decomposes them with the formation of amines (p. 160) (*Berichte*, 17, 574).

The aldehydes also unite with p-amido-dimethylaniline (*Berichte*, 17, 2939). On boiling the aldehydes with an alcoholic solution of resorcinol and a trace of hydrochloric acid insoluble compounds are produced. The ketones do not react under these conditions (*Berichte*, 19, 1389). Mercaptals are formed by the union of the mercaptans with the aldehydes (and ketones).

1. ALDEHYDES OF THE PARAFFIN SERIES, $C_nH_{2n}O$.

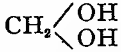
1. **Methyl Aldehyde**, CH_2O, called **Formic Aldehyde**, or oxymethylene, is only known in aqueous solution and in gaseous form. It arises in the oxidation of methyl alcohol, if its vapors

mixed with air be conducted over an ignited platinum spiral; also by the distillation of calcium formate and upon digesting methylal with sulphuric acid.

It is noteworthy that formic aldehyde appears to exist in the plant cells which contain chlorophyll (*Berichte*, **14**, 2147).

Preparation: (1) Mix methylal or other acetals with sulphuric acid, add water and distil. Aqueous formic aldehyde passes over (*Berichte*, **19**, 1841); (2) conduct a mixture of air and the vapors of methyl alcohol over a platinum spiral heated to redness (Hofmann). If a copper spiral be used a solution will be obtained, containing 30 to 40 per cent. formic aldehyde (*Journ. prk. Ch.*, **33**, 321. *Berichte*, **19**, 2133; **20**, 144; *Annalen*, **243**, 335).

The dilute solution may be concentrated by distillation. But little aldehyde is expelled in this way. When the solution is very concentrated and it is allowed to evaporate over sulphuric acid at a low temperature, or in a vacuum, paraformaldehyde separates (*Berichte*, **16**, 917, and **19**, 2135). To determine the quantity of formic aldehyde present in a solution digest the latter with ammonia, when hexamethyleneamine (p. 193) will be formed, and the excess of ammonia can be determined with sulphuric acid in the presence of litmus (*Berichte*, **22**, 1565, 1929). Or the liquid can be evaporated below 50° to dryness and the residue, hexamethyleneamine weighed (*Legler*, *Berichte*, **16**, 1333).

The concentrated aqueous solution of formic acid not only contains volatile CH_2O, but also the hydrate  $CH_2\langle{}^{OH}_{OH}$, *i. e.*, hypothetical methylene glycol, and non-volatile polyhydrates, *e. g.*, $(CH_2)_2O(OH)_2$, corresponding to polyethylene glycols. Therefore the determinations of the molecular weight of the solution, by the method of Raoult, have yielded different values (*Berichte*, **21**, 3503; **22**, 472). On complete evaporation of the solution the hydrates condense to the solid anhydride $(CH_2O)_n$, paraformaldehyde.

Hydrogen sulphide precipitates formic aldehyde from its aqueous solution completely as trithiomethylene (see below). It unites with ammonium to hexamethyleneamine, $(CH_2)_6N_4$ (see below). When heated with sodium hydroxide it yields methyl alcohol and formic acid: $2CH_2O + H_2O = CH_4O + CH_2O_2$. The alkalies or alkaline earths in dilute solution convert formic aldehyde into methylenenitan and formose; these substances resemble the sugars.

Paraformaldehyde, $(CH_2O)_3$, formerly called **Trioxymethylene**, is obtained by the action of silver oxide upon methene di-iodide, or by heating methene diacetyl ester with water, to 100°. It is best prepared by distilling glycollic acid with a little concentrated sulphuric acid. It is most easily obtained by the condensation of formic aldehyde (see above). It is a white, indistinctly crystalline mass. It sublimes below 100°. The sublimed compound melts at 171°. The vapors have the formula CH_2O which corresponds to their density. When cooled they again condense to the trimolecular form. When paraformaldehyde is heated with water to 130° it changes to the simple molecule CH_2O.

When paramethaldehyde is heated with a trace of sulphuric acid to 120° in a sealed tube it is changed into the isomeric *Trioxymethylene*, $(CH_2O)_3$, crystallizing in long needles and melting at 60°. Its vapor density corresponds to the formula $C_3H_6O_2$ (*Berichte*, **17**, Ref. 567).

When hydrogen sulphide is conducted into the aqueous solution of CH_2O, condensed oxysulphydrides, with exceedingly disagreeable odor, are produced. If these are boiled with concentrated hydrochloric acid, water splits off, and *Trithiomethylene, Trithioformaldehyde*, $C_3H_6S_3 = CH_2\left\langle\begin{matrix}S.CH_2\\S.CH_2\end{matrix}\right\rangle S$, results. When pure it is perfectly inodorous, and *Trimethylene-trisulphone*, $CH_2\left\langle\begin{matrix}SO_2.CH_2\\SO_2.CH_2\end{matrix}\right\rangle SO_2$ (*Berichte*, 23, 60, 71), is produced when trithioformaldehyde is oxidized with potassium permanganate.

Another polymeric *Thiomethylene*, $(CH_2S)_n$, obtained from hexamethyleneamine, results at 176° (*Berichte*, 19, 2344), and crystallizes in shining white needles, fusing at 216°, and subliming readily. The vapor density answers to the formula $C_3H_6S_3$.

Hexamethyleneamine, $(CH_2)_6N_4$, is obtained by the action of ammonia on aqueous formic aldehyde (*Berichte*, 19, 1842). It is readily soluble in water and crystallizes from alcohol in shining rhombohedra. It sublimes in vacuo without decomposition. For the molecular weight of the solution see *Berichte*, 21, 1570. It is resolved into CH_2O and ammonia again by distillation with sulphuric acid. It is a monacidic base, but does not react with litmus (*Berichte*, 22, 1929). It unites with the alkyl iodides (*Berichte*, 19, 1842). Formic aldehyde also combines with phenylhydrazine, amines and anilines (*Berichte*, 18, 3300). Nitrous acid produces peculiar nitrosamines (*Berichte*, 21, 2883).

2. **Acetaldehyde**, $C_2H_4O = CH_3.CHO$, is formed according to the methods described above, but is generally prepared by the oxidation of ethyl alcohol with potassium bichromate and dilute sulphuric acid. Commercial aldehyde, and especially that employed in the preparation of aniline colors, is obtained from the first runnings in the rectification of spirit. It is made, too, in the oxidation of alcohol in running over wood charcoal. Its production from vinylsulphuric acid, $SO_4H(C_2H_3)$, (from acetylene), by boiling with water, is of theoretical interest. (Compare p. 134.)

Preparation.—Pour 12 parts H_2O over 3 parts $K_2Cr_2O_7$, and then gradually add, taking care to have the solution cooled, a mixture of 4 parts concentrated H_2SO_4, and 3 parts alcohol (90 per cent.); the heat of a water-bath is now applied, and the vapors that escape are condensed in a receiver. The resulting distillate, consisting of alcohol, aldehyde and acetal, is next heated to 50°, and the escaping aldehyde vapors conducted into ether, and this solution saturated with dry NH_3, when the aldehyde-ammonia, $C_2H_4O.NH_3$, will separate in a crystalline form. Pure aldehyde may be obtained from this by distilling it together with dilute sulphuric acid. The aldehyde vapors are freed from moisture by conducting them over heated calcium chloride.

Acetaldehyde is a mobile, peculiar-smelling liquid. It boils at 20.8°, and has a sp. gr. of 0.8009 at 0°. It is miscible in all proportions with water, ether and alcohol. It slowly oxidizes to acetic acid when exposed to the air. From an ammoniacal silver solution it immediately throws out metallic silver as a mirror-like deposit. Nascent hydrogen transforms aldehyde into ethyl alcohol. PCl_5 and PBr_5 convert it into $CH_3.CHCl_2$ and $CH_3.CHBr_2$ (p. 189).

Ethylaldoxime, $CH_3.CH:N.OH$, isonitrosoethane, produced by the action of hydroxylamine upon acetaldehyde (p. 191), boils at 115°, possesses an aldehyde-like odor, and is miscible with water, alcohol and ether.

Ethylidene-phenylhydrazone, $CH_3.CH:N:NH.C_6H_5$, from aldehyde and phenylhydrazine, is a liquid boiling near 250°.

When an ethereal solution of aldehyde is saturated with dry ammonia, aldehyde-ammonia, $C_2H_4O.NH_3$ (p. 189), separates out. This compound is readily soluble in water, but not so readily in alcohol, and crystallizes in large, glistening rhombohedra, which fuse at 70°–80°, and vaporize undecomposed in a vacuum.

On shaking aldehyde with aqueous solutions of acid alkaline sulphites, crystalline compounds, *e.g.*, $CH_3.CHO.HSO_3K$ (see p. 189), separate. If these be heated together with acids, they break up into their components.

With anhydrous hydrocyanic acid, aldehyde yields $CH_3.CH(OH)CN$ (see p. 190), a liquid readily soluble in water and alcohol, and boiling with slight decomposition at 183°. The alkalies break it up into its components, and concentrated hydrochloric acid converts it into lactic acid.

Polymeric Aldehydes. Small quantities of acids (HCl, SO_2) or salts (especially $ZnCl_2$) convert aldehyde at ordinary temperatures into **paraldehyde,** $(C_2H_4O)_3$, (see p. 192); the change (accompanied by evolution of heat and contraction) is particularly rapid, if a few drops of sulphuric acid be added to the aldehyde. Paraldehyde is a colorless liquid boiling at 124°, and of sp. gr. 0.9943 at 20°. It dissolves in about 12 vols. H_2O, and is, indeed, more soluble in the cold than in the warm liquid. This behavior would point to the formation of a hydrate. The vapor density agrees with the formula $C_6H_{12}O_3$. When distilled with sulphuric acid ordinary aldehyde is generated.

Metaldehyde, $(C_2H_4O)_n$, is produced by the same reagents (see above) acting on ordinary aldehyde at temperatures below 0°. It is a white crystalline body, insoluble in water, but readily dissolved by hot alcohol and ether. If heated to 112°–115° it sublimes without previously melting, and passes into ordinary aldehyde with only slight decomposition. When heated in a sealed tube the change is complete.

There are many reagents that change meta- and paraldehydes to ordinary aldehyde and its derivatives; *e. g.*, PCl_5 converts them into ethidene dichloride, $CH_3.CHCl_2$. They do not combine with NH_3 or alkaline bisulphites, do not reduce silver solutions, nor do they give an aldoxime with hydroxylamine (p. 191). Paraldehyde is not attacked by sodium, even when assisted by heat. These facts go to prove that in the polymeric aldehydes, the aldehyde radicals are linked by oxygen atoms (see p. 190), the same as the alkyls in the ethers. Their refractive power and their specific volume would also indicate that the oxygen atoms present in them are united to carbon by but one affinity.

Condensation Products. When acetaldehyde is heated with zinc chloride, water separates and crotonaldehyde is produced:—

$$\underbrace{CH_3.CHO + CH_3.CHO}_{\text{2 Mols. Aldehyde.}} = \underbrace{CH_3.CH:CH.CHO}_{\text{Crotonaldehyde.}} + H_2O.$$

By long contact with dilute sulphuric acid, aldehyde first becomes aldol (see this):—

$$CH_3.CHO + CH_3.CHO = \underbrace{CH_3.CH(OH).CH_2.CHO}_{\text{Aldol.}},$$

and this when heated with zinc chloride, gives up water and passes into crotonaldehyde:—

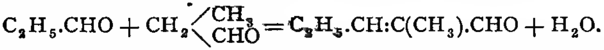
$$CH_3.CH(OH).CH_2.CHO = CH_3.CH{:}CH.CHO + H_2O.$$

When chlorine is conducted into cold aldehyde chlor-crotonaldehyde, $CH_3.CH{:}CCl_2.CHO$, and trichlorbutyraldehyde, $C_4H_5Cl_3O$ (p. 197), are formed, and by the action of nascent hydrogen (sodium amalgam) there results butylene glycol, $CH_3.CH.OH.CH_2.CH_2.OH$.

Sulphuric acid, sodium acetate (*Berichte*, **16**, 786), and alkalies (sodium hydroxide and baryta water), exert the same power of condensation as zinc chloride and hydrochloric acid.

Such a union of two or more molecules, by the linking of carbon atoms (followed either with or without water separation), and the formation of complicated carbon chains, is ordinarily termed *condensation,* distinction being made at the same time between the *aldol condensation* and genuine *aldehyde condensation,* in which an exit of water does occur.

In the case of the higher aldehydes (also ketones), the condensation is so made that the oxygen of aldehyde unites with the hydrogen of a CH_2 group. Thus, from propylaldehyde we get methylethyl acroleïn:—



$$C_2H_5.CHO + CH_2\langle\begin{smallmatrix}CH_3\\CHO\end{smallmatrix} = C_2H_5.CH{:}C(CH_3).CHO + H_2O.$$

The aldehydes act in a perfectly similar manner upon the esters of malonic acid, $CH_2(CO_2R)_2$, acetic acid and analogous compounds (*Annalen*, **218**, 121).

Another very remarkable condensation is sustained by the aldehydes through the action of ammonia (heating of aldehyde-ammonias); nitrogenous bases (pyridine bases) are produced.

Substituted Aldehydes. These are obtained by the action of chlorine upon acetaldehyde or ethyl alcohol, the latter being simultaneously oxidized to aldehyde. The only pure compound that can be formed in this manner is the final chlorination product, *trichloraldehyde.*

Monochloraldehyde, $CH_2Cl.CHO$, is obtained pure by distilling monochloracetal, $CH_2Cl.CH(O.C_2H_5)_2$, with anhydrous oxalic acid. It is a liquid that boils at 85°, and polymerizes very rapidly to a white mass (*Berichte*, **15**, 2245). When oxidized it yields monochloracetic acid; with CNH and hydrochloric acid it becomes β-chlorlactic acid.

Dichloraldehyde, $CHCl_2.CHO$, is produced in the distillation of dichloracetal, $CHCl_2.CH(O.C_2H_5)_2$, with concentrated sulphuric acid. It boils at 88°–90°, and when preserved, changes into a solid polymeric modification. The hydrate, $CHCl_2.CHO + H_2O$, corresponding to chloral hydrate, fuses at 57° and boils at 110°. When it is oxidized with HNO_3 dichloraldehyde is converted into dichloracetic acid. It yields dichlorlactic acid by the action of CNH and hydrochloric acid.

Trichloracetaldehyde, $CCl_3.CHO$, **Chloral**, is best prepared by conducting chlorine into alcohol and distilling the crystalline product with sulphuric acid. It is an oily, pungent-smelling liquid, which boils at 97°, and has the sp. gr. 1.541 at 0°. With NH_3, CNH, acid sulphites of the alkali metals, etc., chloral furnishes compounds similar to those of ordinary aldehyde; it also reduces an ammoniacal silver solution. When kept for some time it passes into a solid polymeride. It yields trichloracetic acid when oxidized by HNO_3. When heated with alkalies it breaks up into chloroform and a formate:—

$$CCl_3.CHO + KOH = CCl_3H + CHO.OK.$$

When it combines with a small quantity of water chloral changes to

Chloral Hydrate, $C_2HCl_3O.H_2O = CCl_3.CH<\begin{matrix}OH\\OH\end{matrix}$, which consists of large monoclinic prisms, fusing at 57° and distilling at 96–98°. The vapors dissociate into chloral and water. Chloral hydrate dissolves readily in water, possesses a peculiar odor and a sharp, biting taste; when taken internally it produces sleep. Concentrated sulphuric acid resolves the hydrate into water and chloral.

Chloral and alcohol combine to **Chloral Alcoholate**,—trichlorethidene ethyl ether—$CCl_3.CH<\begin{matrix}O.C_2H_5\\OH,\end{matrix}$ a crystalline solid, fusing at 56° and boiling at 114–115°. When acetyl chloride is allowed to act upon the preceding derivative the acetyl ester, trichlorethidene ethyl acetin, is produced. This boils at 198°. Concentrated sulphuric acid reproduces chloral from the alcoholate.

Acetic anhydride and chloral yield trichlorethidene diacetate, $CCl_3.CH(O.C_2H_3O)_2$, which boils at 221°. It unites with ammonia to form **chloral-ammonia**,—trichlorethidene hydramine—$CCl_3.CH<\begin{matrix}OH\\NH_2\end{matrix}$, melting at 63°. With prussic acid it furnishes **chloral-cyanhydrate**, $CCl_3.C^H<\begin{matrix}OH\\CN,\end{matrix}$ a crystalline derivative, fusing at 61–62°, and passing into trichlorlactic acid when treated with hydrochloric acid.

Dibromacetaldehyde, $CHBr_2.CHO$, obtained by the bromination of aldehyde or paraldehyde, is a liquid, boiling at 142°. After standing some time it becomes solid—a polymeric modification. It yields a crystalline **hydrate** with water. It combines with CNH to form the compound, $CHBr_2.CH<\begin{matrix}CN\\OH\end{matrix}$, from which dibromlactic acid may be obtained.

Tribromaldehyde, $CBr_3.CHO$, **Bromal**, is perfectly analogous to chloral. It boils at 172–173°, and with water forms a solid hydrate fusing at 53°. The **alcoholate** melts at 44° and decomposes at 100°. Heated with alkalies bromal breaks up into bromoform and a formate. It yields a cyanide, $CBr_3.CH<\begin{matrix}OH\\CN,\end{matrix}$ with CNH and this hydrochloric acid converts into tribromlactic acid.

Iodo-acetaldehyde, $CH_2I.CHO$, is made by acting on aldehyde with iodine or iodic acid. It is an oily liquid, with a very disgusting odor (*Berichte*, **22**, Ref. 561). Silver cyanide converts it into cyanaldehyde, $C_2H_3(CN)O$ (*Berichte*, **22**, Ref. 563).

Sulphur Compounds.—On passing hydrogen sulphide into an aqueous solution of aldehyde the reaction proceeds in the same manner as with formic aldehyde. In the presence of hydrochloric acid two isomeric trithioaldehydes, $(C_2H_4S)_3$, are produced. They crystallize in long needles and prisms. *a-Trithioaldehyde* melts at 101°, and the *β*- modification at 120°. Both boil about 245°. Concentrated H_2SO_4, or acetylchloride, converts the *a*- into the *β*- variety. When oxidized with $KMnO_4$ both varieties yield the same *Trialdehyde-trisulphone*, $(CH_3.CH)_3(SO_2)_3$ (*Berichte*, **22**, 2600; **23**, 60).

Thialdin, $C_6H_{13}NS_2$, separates on conducting H_2S into an aqueous solution of aldehyde-ammonia. It consists of large, colorless crystals, fusing at 43°. It is a monacidic, secondary base, and may be viewed as a trithioaldehyde in which an atom of sulphur is replaced by the imide group, inasmuch as it can also be made by allowing ammonia to act upon trithioaldehyde. In a similar manner methylamine produces *Methylthialdin*, $(C_2H_4)_3S_2(N.CH_3)$, melting at 19° (*Berichte*, **19**, 2378).

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3. **Propionic Aldehyde**, $C_3H_6O = C_2H_5.CHO$, is obtained from normal propyl alcohol, and by the dry distillation of calcium propionate and formate. It is very similar to acetaldehyde, boils at 49°, and has a sp. gr. 0.8066 at 20°. It is soluble in 5 vols. H_2O at 20°. With PCl_5 it yields $C_2H_5.CHCl_2$.

Propyl Aldoxime, $C_2H_5.CH{:}N.OH$ (see p. 191), boils at 131°.

***β*-Chlorpropionic Aldehyde**, $CH_2Cl.CH_2.CHO$. This is produced when HCl is added to acroleïn; it fuses at 35°, and, when distilled, again breaks up into acroleïn and HCl. Nitric acid oxidizes it to *β*-chlorpropionic acid.

4. **Butyraldehydes**, $C_4H_8O = C_3H_7.CHO$. Two isomeric aldehydes of this form exist; they correspond to the two primary butyl alcohols.

(1) **Normal Butyraldehyde**, $CH_3.CH_2.CH_2.CHO$, from normal butyl alcohol and normal butyric acid (*Berichte*, **18**, 3364), is a liquid boiling near 75°, and has a sp. gr. 0.8170 at 20°. It dissolves in 27 parts H_2O, and oxidizes readily to butyric acid. Heated with alcoholic ammonia it yields the base **paraconine**, $C_8H_{15}N$, boiling at 170° and very similar to **conine**, $C_8H_{17}N$. The isomeric paraconine obtained from isobutyraldehyde boils at 146°.

***β*-Chlorbutyraldehyde**, $CH_3.CHCl.CH_2.CHO$, is produced from crotonaldehyde, $CH_3.CH{:}CH.CHO$, by the addition of HCl, and consists of needles, fusing at 96°. Nitric acid oxidizes it to *β*-chlorbutyric acid.

Trichlorbutyraldehyde, $CH_3.CHCl.CCl_2.CHO$, formerly obtained from crotonaldehyde, $C_4H_5Cl_3O$, is produced by the action of chlorine upon acetaldehyde or paraldehyde, the first product being chlorcrotonaldehyde, $CH_3.CH{:}CCl.COH$ (p. 195), which further unites with Cl_2, yielding butylchloral (*Annalen*, **219**, 374).

The latter compound, like the ordinary chloral, is a heavy, oily liquid, boiling at 163–165°, and forming with water the hydrate, $C_4H_5Cl_3O + H_2O$; this last crystallizes in tablets, fusing at 78°. The alkalies decompose butyl chloral into acetic acid, potassium chloride and allylene dichloride, $CH_3\,CCl{:}CHCl$. It yields a trichlorbutyric acid when oxidized with nitric acid.

(2) **Isobutyraldehyde,** $(CH_3)_2CH.CHO$, obtained from fermentation butyl alcohol and calcium isobutyrate, has the sp. gr. 0.7898 at 20°, and boils at 63°. It dissolves in nine volumes of water at 20°. A small quantity of concentrated sulphuric acid converts it into **Para-isobutyraldehyde,** $(C_4H_8O)_3$, which crystallizes in brilliant needles, melting at 60°, and boiling at 194°.

5. *Amyl Aldehydes,* $C_5H_{10}O = C_4H_9.CHO$, Valeraldehydes. There are four possible isomerides; two of these are known:—

Normal Amyl Aldehyde, $(CH_3)(CH_2)_3CHO$, from valeric acid, boils at 102°. **Isoamyl Aldehyde,** $(CH_3)_2.CH.CH_2.CHO$, from the amyl alcohol of fermentation and from isovaleric acid, is a liquid, with fruit-like odor, boiling at 92°, and polymerizing readily. When oxidized it becomes isovaleric acid. On heating with alcoholic ammonia to 150° it yields two basic compounds, *valeridine,* $C_{10}H_{19}N$, and *valeritrine,* $C_{15}H_{27}N$, which boils near 250°.

Normal Hexyl Aldehyde, $C_6H_{12}O = C_5H_{11}.CHO$, **Caproyl Aldehyde,** from caproic acid, boils at 128°. **Normal Heptyl Aldehyde,** $C_7H_{14}O$, **œnanthylic aldehyde,** or **œnanthol,** is produced along with hendecatoic acid in the distillation of castor-oil, best under diminished pressure. It is a pungent-smelling liquid, boiling at 153–154°. It becomes normal heptylic acid, $C_7H_{14}O_2$, when oxidized with dilute nitric acid (1 : 2 vols. H_2O).

The higher aldehydes are most advantageously prepared by the distillation, under diminished pressure, of the barium salts of the corresponding fatty acids with barium formate (*Berichte,* 16, 1716). Like their acids, they all have normal structure. They can be boiled without decomposition only under a somewhat diminished pressure.

Decatoic Aldehyde, $C_{10}H_{20}O$, **Capric Aldehyde,** obtained from capric acid, boils at 106° under a pressure of 15 mm.

Dodecatylic Aldehyde, $C_{12}H_{24}O$, **Lauric Aldehyde,** from lauric acid, crystallizes in shining tablets, fusing at 44.5°, and boiling at 142° (22 mm.).

Tetradecatylic Aldehyde, $C_{14}H_{28}O$, **Myrisitaldehyde,** made from myristic acid, melts at 52.5°, and under 22 mm. pressure boils at 168° C.

Hexdecatylic Aldehyde, $C_{16}H_{32}O$, **Palmitic Aldehyde,** from palmitic acid, fuses at 58.5°, and under 22 mm. pressure boils at 192° C.

Octdecatylic Aldehyde, $C_{18}H_{36}O$, **Stearaldehyde,** consists of tablets having a bluish lustre. It fuses at 63.5°, and boils at 192° C. (under 22 mm. pressure).

2. UNSATURATED ALDEHYDES, $C_nH_{2n-2}O$.

These derivatives bear the same relation to the alcohols of the allyl series as the aldehydes just considered bear to the alcohols $C_nH_{2n+2}O$, of the saturated hydrocarbons. Inasmuch as they are unsaturated compounds they are capable of directly saturating two affinities.

The first and lowest member of the series is:—

Acrylaldehyde, $C_3H_4O = CH_2:CH.CHO$, or **Acroleïn.** This is produced by the oxidation of allyl alcohol and by the distillation of glycerol or fats:—

$$\underset{\text{Glycerol.}}{C_3H_5(OH)_3} = C_3H_4O + 2H_2O.$$

One part of glycerol is distilled with two parts of acid potassium sulphate. The distillate is redistilled over lead oxide (*Annalen, Suppl.*, 3, 180).

Acroleïn is a colorless, mobile liquid, boiling at 52°, and possessing a sp. gr. of 0.8410 at 20°. It has a pungent odor and attacks the mucous membranes in a frightful manner. The odor of burning fat is occasioned by acroleïn. It is soluble in 2–3 parts water. It reduces an ammoniacal silver solution, with formation of a mirror-like deposit, and when exposed to the air it oxidizes to acrylic acid. It does not combine with primary alkaline sulphites. Nascent hydrogen converts it into allyl alcohol.

Phosphorus pentachloride converts acroleïn into propylene dichloride, $CH_2:CH.CHCl_2$, boiling at 84° C. With hydrochloric acid it yields β-chlorpropionic aldehyde (p. 197). With bromine it yields a dibromide, $CH_2.Br.CHBr.CHO$, which becomes β-dibrompropionic acid upon oxidation.

When preserved, acroleïn passes into an amorphous, white mass (*disacryl*). On warming the HCl compound of acroleïn (see above) with alkalies or potassium carbonate *metacroleïn* is obtained. The vapor density of this agrees with the formula $(C_3H_4O)_3$. It crystallizes from alcohol in tablets, fusing at 45–46°, and dissociating at 160° C.

Ammonia changes acroleïn to the so-called *acroleïn-ammonia*, $C_6H_9NO + \frac{1}{2}H_2O$:—

$$2C_3H_4O + NH_3 = C_6H_9NO + H_2O.$$

This is a yellowish mass that on drying becomes brown, and forms amorphous salts with acids. It yields *picoline*, C_6H_7N (methyl-pyridine, $C_5H_4N.CH_3$), when distilled.

Crotonaldehyde, $C_4H_6O = CH_3.CH:CH.CHO$, is obtained by the condensation of acetaldehyde (p. 194) when heated with dilute hydrochloric acid, with water and zinc chloride, or with a sodium acetate solution, to 100° C. (*Berichte*, 14, 514 and 516):—

$$CH_3.CHO + CH_3.CHO = CH_3.CH:CH.CHO + H_2O.$$

It is also produced when the sulphuric acid solution of bromethylene is boiled with water (see p. 134). Crotonaldehyde is a liquid with irritating odor, soluble in water; at 0° it has a sp. gr. of 1.033, and boils at 104–105°. On exposure to the air it oxidizes to crotonic acid; it reduces silver oxide. It combines with hydrochloric acid to form β-chlorbutyraldehyde (p. 197); on standing with hydrochloric acid it unites with water and becomes aldol. Iron and acetic acid change it to croton-alcohol, butyraldehyde and butyl alcohol.

a-**Chlorcrotonaldehyde**, $CH_3.CH:CCl.CHO$, is a by-product in the preparation of butyl-chloral, and may also be obtained by the condensation of aldehyde with monochloraldehyde. It is a pungent-smelling oil, boiling at 150°. It combines directly with two atoms of chlorine to butyl chloral (p. 197).

When the alcoholic solution of acetaldehyde-ammonia is heated to 120°, **Crotonal-ammonia**, $C_8H_{13}NO$ (**Oxtetraldine**), is produced. This bears the same relation to crotonaldehyde that acroleïn-ammonia does to acroleïn. It is a brown amorphous mass, yielding amorphous salts with acids. When heated it breaks up into water and collidine, $C_8H_{11}N$ = trimethylpyridine, $C_5H_2N(CH_3)_3$.

Methyl-ethyl Acroleïn, $C_2H_5.CH:C(CH_3).CHO$, is produced by the condensation of propionic aldehyde (p. 195), and boils at 137° C.

KETONES.

The ketones are characterized by the group CO in combination with two alkyls. They share many analogies with the aldehydes, indicated by the similar methods of production (see p. 186). We have the following specific methods for their formation :—

1. The action of the zinc alkyls (1 molecule) upon the chlorides of the acid radicals (2 molecules) :—

$$\underset{\text{Propionyl Chloride.}}{2C_2H_5.COCl} + Zn(CH_3)_2 = \underset{\text{Methyl-ethyl Ketone.}}{2C_2H_5.CO.CH_3} + ZnCl_2,$$

$$2C_2H_5.COCl + Zn(C_2H_5)_2 = \underset{\text{Diethyl Ketone.}}{2C_2H_5.CO.C_2H_5} + ZnCl_2.$$

To the zinc alkyl (1 molecule), cooled by ice, there are added drop by drop at first, then rapidly, 2 molecules of the acid chloride, and the product of the reaction is immediately decomposed by a large quantity of water. The reaction is similar to that occurring in the formation of the tertiary alcohols (p. 120). At first the same intermediate product is produced :—

$$CH_3.COCl + Zn(C_2H_5)_2 = CH_3.C\left\{\begin{array}{l} C_2H_5 \\ O.Zn.C_2H_5, \\ Cl \end{array}\right.$$

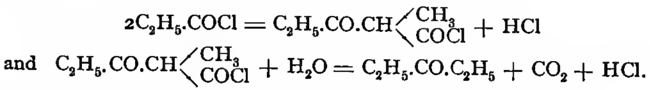
which (with a second molecule of the acid chloride) afterwards yields the ketone :—

$$CH_3.C\left\{\begin{array}{l} C_2H_5 \\ O.Zn.C_2H_5 \\ Cl \end{array}\right. + CH_3.COCl = 2CH_3.CO.C_2H_5 + ZnCl_2.$$

In many cases, especially in the preparation of the pinacolines, it is, however, more advantageous to employ double the quantity of the zinc alkyl (1 molecule to 1 molecule acid chloride) which will serve to dilute the mixture (*Annalen*, 188, 144); in this manner the intermediate product forms the ketone with water, and there occurs a simultaneous evolution of paraffins. The aqueous solution is distilled, and the ketone separated from it by means of soda.

2. By the action of anhydrous ferric chloride upon the acid radicals. At first hydrochloric acid gas is evolved and an intermediate product formed, which is

changed by water and evolution of CO_2 into a ketone (*Berichte*, 22, Ref. 141). Propinyl chloride, treated as above, yields diethyl ketone:—



$$2C_2H_5.COCl = C_2H_5.CO.CH{<}\genfrac{}{}{0pt}{}{CH_3}{COCl} + HCl$$

$$\text{and}\quad C_2H_5.CO.CH{<}\genfrac{}{}{0pt}{}{CH_3}{COCl} + H_2O = C_2H_5.CO.C_2H_5 + CO_2 + HCl.$$

Butyryl chloride, $C_3H_7.COCl$, yields dipropyl ketone, $C_3H_7.CO.C_3H_7$.

3. The oxidation of the acids of the lactic series with secondary alkyls, by means of bichromate of potash and dilute sulphuric acid (see p. 188): —

$$\underset{\text{Oxyisobutyric Acid.}}{(CH_3)_2C(OH).CO_2H} + O = \underset{\text{Dimethyl Ketone.}}{(CH_3)_2CO} + CO_2 + H_2O.$$

4. The decomposition of the aceto-acetic acids and their esters (see these):—

$$CH_3.CO.CH_2.CO_2.C_2H_5 + H_2O = CH_3.CO.CH_3 + CO_2 + C_2H_5.OH.$$

The ketones are also produced in the dry distillation of wood, sugar, and many other carbon compounds.

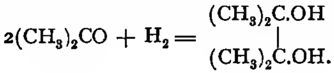
The names of the ketones are derived by combining the names of the alkyls with the syllable *ketone*. A. Baeyer regards the ketones as keto-substitution products of the hydrocarbons resulting from the replacement of two hydrogen atoms by one atom of oxygen. Accordingly dimethyl ketone, $CH_3.CO.CH_3$, is called ketopropane, ethyl-methyl ketone, $C_2H_5.CO.CH_3$, α-ketobutane, etc. (*Berichte*, 19, 160).

The ketones are generally ethereal-smelling, volatile liquids, insoluble in water. They do not reduce ammoniacal silver solutions. They combine, like aldehydes, with the primary alkaline sulphites; but it appears that only those of the higher ketones, in which the group CO is in combination with the methyl group, are adapted to this reaction. Boiling alkaline carbonates again separate the ketone from these compounds (p. 190). Hence, these reactions serve both for the isolation and the purification of these derivatives.

Nascent hydrogen (sodium amalgam) converts them into secondary alcohols:—

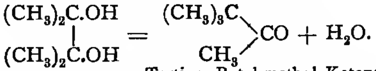
$$(CH_3)_2CO + H_2 = (CH_3)_2CH.OH.$$

At the same time there occurs here, as with the aldehydes (p. 194), a condensation of the ketone molecule, accompanied by the formation of dihydric alcohols:—



$$2(CH_3)_2CO + H_2 = \begin{array}{l}(CH_3)_2C.OH\\ \quad | \\ (CH_3)_2C.OH.\end{array}$$

These are termed *pinacones*. When heated with acids they sustain a peculiar transposition of atoms, and are converted into ketones:—



$$\begin{matrix}(CH_3)_2C.OH\\ |\\ (CH_3)_2C.OH\end{matrix} = \begin{matrix}(CH_3)_3C\diagdown\\ \\ CH_3\diagup\end{matrix}CO + H_2O.$$

Tertiary Butyl-methyl Ketone.

Such ketones, containing a tertiary alkyl group, are designated *pinacolines*. They may be synthesized by the action of zinc alkyls upon the chlorides of such fatty acids as contain tertiary alkyls:—

$$\underset{\text{Trimethyl Acetyl Chloride.}}{(CH_3)_3C.COCl} \text{ yields } \underset{\text{Pinacoline.}}{(CH_3)_3C.CO.CH_3}.$$

The ketones also unite with HCN, forming oxycyanides, *e.g.*, $(CH_3)_2C(OH).CN$ (see *Berichte*, 15, 2306), from which the corresponding oxyacids may be obtained (see p. 190). Similarly, acetone in the presence of caustic soda combines with chloroform, yielding *acetone chloroform*, $(CH_3)_2C\begin{matrix}\diagup OH\\ \diagdown CCl_3.\end{matrix}$ This, too, can be converted into the corresponding oxyacid.

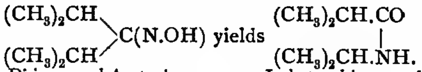
All the ketones (like the aldehydes, p. 191) combine with hydroxylamine, and become oximid- or isonitroso-compounds, called *acetoximes*, or *ketoximes* (see p. 205):—

$$(CH_3)_2CO + H_2N.OH = (CH_3)_2C{:}N.OH + H_2O.$$

To prepare the ketoximes the ketones are allowed to stand for some time with hydroxylamine hydrochloride. The reaction is accelerated by heating in a water-bath, or in a sealed tube. Frequently the reaction will only occur in feebly alkaline solutions. Soda or caustic soda is then added in equivalent amount. At times a great excess of caustic soda (3 mol.) must be added (*Berichte*, 22, 605). Instead of using hydroxylamine hydrochloride, potassium hydroxylamine-disulphonate (reducing salt) may be used (*Annalen*, 241, 187). This salt is obtained by acting upon sodium nitrite with monosodium sulphite.

The acetoximes, like the aldoximes, are split up into their components when boiled with acids. They are similarly transformed into amines by sodium amalgam and acetic acid (p. 160). They are distinguished from the aldoximes in that the latter yield nitriles with acetyl chloride, while the acetoximes, under like influence, form oils with peculiar odor. Nitrogen tetroxide converts the ketoximes into pseudo-nitrols.

Acetoximes with tertiary hydrogen atoms, readily suffer molecular rearrangements under the influence of acetyl chloride (*Berichte*, 20, 506):—



$$\begin{matrix}(CH_3)_2CH\diagdown\\ \\ (CH_3)_2CH\diagup\end{matrix}C(N.OH) \text{ yields } \begin{matrix}(CH_3)_2CH.CO\\ |\\ (CH_3)_2CH.NH.\end{matrix}$$

Di-isopropyl Acetoxime. Isobutyryl-isopropyl Amine.

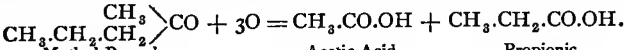
All ketoximes sustain an analogous transformation by the action of hydrochloric, sulphuric or acetic acid. Thus, methyl-propyl-ketoxime yields acetopropylamine (*Beckmann*, 21, 2530):—

$$C_3H_7.C(NOH).CH_3 = C_3H_7.NH.CO.CH_3.$$

All bodies possessing the ketone group CO (or the aldehyde group), *e. g.*, the ketonic acids and alcohols, react with hydroxylamine in a manner similar to that of the ketones. Some acid anhydrides, *e.g.*, phthalic anhydride (*Berichte*, 16, 1780), do the same. This is not, however, the case with the lactones and alkylen oxides. The diketones, such as glyoxal, CHO.CHO, are capable of a double reaction with hydroxylamine, yielding compounds known as *acetoximic acids* or glyoximes. The ketones react more readily with phenylhydrazine, forming crystalline compounds (the hydrazones) than with hydroxylamine (*Berichte*, 17, 576; 16, 661; 20, 513).

Boiling nitric acid converts the ketones into dinitroparaffins. In this reaction the nitro-groups attach themselves to the higher alkyl of the mixed ketones. The ketones (like the aldehydes, p. 191) form mercaptols with the mercaptans.

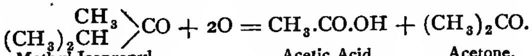
The ketones cannot be directly oxidized. When they are boiled with $K_2Cr_2O_7$ and dilute sulphuric acid, they break up in such a manner that the CO group passes out in combination with the lower alkyl, thus producing an acid. Should the other higher alkyl chance to be of a primary character, it, too, will be oxidized to an acid:—



$$\left.\begin{matrix}CH_3\\CH_3.CH_2.CH_2\end{matrix}\right\rangle CO + 3O = CH_3.CO.OH + CH_3.CH_2.CO.OH.$$

Methyl Propyl Ketone. Acetic Acid. Propionic Acid.

When the higher radical is secondary, it first becomes a ketone, and this decomposes further:—



$$\left.\begin{matrix}CH_3\\(CH_3)_2CH\end{matrix}\right\rangle CO + 2O = CH_3.CO.OH + (CH_3)_2CO.$$

Methyl Isopropyl Ketone. Acetic Acid. Acetone.

When the CO group is united to carbon atoms carrying an equal number of hydrogen atoms, it remains with the higher alkyl when decomposition occurs (*Berichte*, 15, 1194). For further details of the decomposition, see *Berichte*, 18, 2266, and Ref. 181.

To oxidize ketones, proceed as follows: dilute a mixture consisting of 1 molecule ketone, 1 molecule $K_2Cr_2O_7$ and 4 molecules H_2SO_4, with 5–10 parts water, and heat the same in a large flask, provided with a long, upright glass tube serving as a condenser. The reaction is complete when the mixture assumes the pure, green color of chromium sulphate (compare *Annalen*, 190, 349):—

$$K_2Cr_2O_7 + 4H_2SO_4 = (SO_4)_3Cr_2 + K_2SO_4 + 4H_2O + 3O.$$

The acids produced are distilled over with water.

A similar decomposition is sustained by the ketones when oxidized by free chromic acid, potassium permanganate, PbO_2, etc. (*Annalen*, 186, 257.)

Dimethyl Ketone, $C_3H_6O = (CH_3)_2CO$, Acetone. In addition to the general methods of formation, acetone is produced by heating chlor- and brom-acetol (p. 101) with water to 160°–180°:—

$$CH_3.CCl_2.CH_3 + H_2O = CH_3.CO.CH_3 + 2HCl;$$

and also by the dry distillation of tartaric and citric acids, sugar, wood, etc. This accounts for its presence in crude wood spirit (p. 124). It is usually obtained by the dry distillation of calcium acetate (p. 187). It occurs, too, in small quantities in the blood and normal urine, while in the urine of those suffering from diabetes it is present in considerable amount.

Of theoretical interest is its formation from β-chlor- and brom-propylene, $CH_3.CBr:CH_2$, when these are heated with water to 200°, or dissolved in sulphuric acid and boiled with water. We would naturally expect an alcohol, $CH_3.C(OH):CH_2$, to be formed here, but a transposition of atoms occurs and acetone results (see p. 134). Acetone is similarly formed from allylene, $CH_3.C \vdots CH$, by action of sulphuric acid or $HgBr_2$ in the presence of water (p. 87).

Acetone is a mobile, peculiar-smelling liquid, boiling at 56.5° and having a sp. gr. of 0.7920 at 20°. It is miscible with water, alcohol and ether. Calcium chloride or other salts set it free from its aqueous solution. The compound it forms with primary sodium sulphite has one molecule of water, and consists of pearly scales, easily soluble in water. Excess of sodium sulphite or alcohol separates it from its solution. When in aqueous solution, sodium amalgam converts it into isopropyl alcohol. The chromic acid mixture oxidizes it to acetic and formic acids, which, as a general thing, are still further oxidized to CO_2 and water:—

$$CH_3.CO.CH_3 + 3O = \underset{\text{Acetic Acid.}}{CH_3.CO.OH} + \underset{\text{Formic Acid.}}{CHO.OH}.$$

The ketones are similarly decomposed when their vapors are conducted over heated soda-lime.

An aqueous acetone solution, mixed with KOH and an iodine solution, yields iodoform (p. 103). This reaction (Lieben) serves to detect acetone even in presence of alcohol (*Berichte*, 13, 1004). All ketones containing the group $CO.CH_3$, do the same (*Berichte*, 14, 1948). In the presence of alcohol it is better to use an iodine solution and ammonia, for then the alcohol will not yield iodoform (Gunning, *Berichte*, 17, Ref. 503). According to the reaction of Weyl and Legal, sodium nitroprusside and sodium hydroxide impart a brown-red color in the presence of acetone (*Berichte*, 17, Ref. 503, and 18, Ref. 195). PCl_5 and PBr_5 convert acetone into chlor- and brom-acetol (p. 101).

ACETONE SUBSTITUTION PRODUCTS result by the direct action of chlorine or bromine upon acetone and by various other methods.

Monochloracetone, $CH_3.CO.CH_2Cl$, is obtained by conducting chlorine into cold acetone (*Berichte*, 19, Ref. 48), or by the action of hypochlorous acid upon monochlor- or monobrom-propylene:—

$$CH_3.CBr{:}CH_2 + ClOH = CH_3.CO.CH_2Cl + HBr.$$

It is a liquid, insoluble in water; its vapors provoke tears.

There are two possible **Dichloracetones**, $C_3H_4Cl_2O$: (α) $CH_3.CO.CHCl_2$ and (β) $CH_2Cl.CO.CH_2Cl$. The first is formed on treating warmed acetone with chlorine, and is obtained from dichloraceto-acetic ester, on boiling the same with hydrochloric acid. (*Berichte*, 15, 1164.) It is an oily liquid, with a sp. gr. of 1.236 at 21°, and boils at 120°. The β-dichloracetone is produced in the oxidation of dichlorhydrin, $CH_2Cl.CH(OH).CH_2Cl$ (see glycerol), with potassium dichromate and sulphuric acid. (*Berichte*, 13, 1701.) It consists of rhombic plates, fusing at 45°, and boiling at 172°–174°.

For other chloracetones, see *Berichte*, 20, Ref. 48.

Symmetrical **Tetrachloracetone**, $CHCl_2.CO.CHCl_2$, is readily obtained by the action of potassium chlorate and hydrochloric acid upon chloranilic acid (*Berichte*, 21, 318) and triamidophenol (*Berichte*, 22, Ref. 666), or of chlorine upon the finest phloroglucin (*Berichte*, 22, 1478). It is a yellow oil. Under a pressure of 725 mm. it boils at 180°. It combines readily with water to the hydrate $C_3H_2Cl_4O + 4H_2O$, crystallizing in large prisms, and melting at 48°. It unites to the corresponding acid with HCN (*Berichte*, 22, Ref. 810). Bromine yields similar substitution products.

Monobromacetone, $CH_2Br.CO.CH_3$, and Symmetrical **Dibromacetone**, $CH_2.Br.CO.CH_2Br$ (*Berichte*, 21, 3288) are oils. They can only be distilled under reduced pressure.

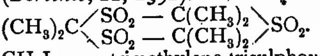
Iodo-Acetone, $CH_3.CO.CH_2I$, is produced when iodine and iodic acid act upon acetone. It is a heavy oil with a disagreeable odor (*Berichte*, 18, Ref. 330).

β-Di-iodoacetone, $CH_2I.CO.CH_2I$, forms when iodine chloride acts upon acetone. It fuses at 62° and decomposes about 120°.

Liquid acetone-chloroform is produced by the action of chloroform and caustic alkali upon acetone. It boils at 170°. In moist air it passes into the isomeric *solid Acetone-chloroform*, $(CH_3)_2.C(OH).CCl_3$ (compare p. 202). This consists of crystals, melting at 97° and boiling at 167°. They have an odor like that of camphor. Aqueous alkalies convert it into oxyisobutyric acid. Two complex acids result in the presence of acetone (*Berichte*, 20, 2449).

Acetone-cyanhydrin, $(CH_3)_2.C(OH).CN$, is obtained from acetone and CNH. It is a liquid, boiling at 120°.

Hydrogen sulphide converts acetone into *Trithioacetone*, $(C_3H_6S)_3$. This is analogous to trithioaldehyde. Colorless needles, melting at 24° and boiling at 230° (*Berichte*, 22, 2592). $KMnO_4$ oxidizes this compound to *Triacetone-trisulphone*,



$(CH_3)_2C{<}\begin{matrix} SO_2 - C(CH_3)_2 \\ SO_2 - C(CH_3)_2 \end{matrix}{>}SO_2$. This also results from the action of NaOH and CH_3I upon trimethylene trisulphone (p. 193) (*Berichte*, 22, 2609; 23, 71).

Hydroxylamine- or Oximido-Derivatives (p. 106 and p. 202). **Acetoxime**, $(CH_3)_2C{:}N.OH$, dimethylacetoxime, formed in the action of hydroxylamine upon acetone (p. 202) (*Berichte*, 20, 1505), is a compound readily soluble in water, alcohol and ether. It fuses at 60° and boils at 135°. Boiling acids regenerate acetone and hydroxylamine.

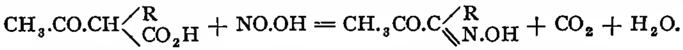
Hypochlorous acid converts acetoxime into an ester, $(CH_3)_2.C:N.O.Cl$. This is a liquid with an agreeable odor. It boils at 134°. It explodes when rapidly heated (*Berichte*, 20, 1505).

The hydroxyl hydrogen present in this compound may be replaced by acid radicals through the agency of acid chlorides or anhydrides. With sodium alcoholate, the sodium derivative results, which yields the alkyl ethers, $(CH_3)_2C:N.OR$, when acted upon by the alkylogens. On boiling these ethers with acids, acetone and alkylized hydroxylamines, NH_2OR (*Berichte*, 16, 170), are produced. The higher acetoximes show a perfectly analogous deportment.

Isonitroso-acetone, $CH_3.CO.CH:N.OH$. This is obtained from the isonitroso-aceto-acetic ester (*Berichte*, 15, 1326). Nitrous acid converts aceto-acetic acid directly into isonitroso-acetone and carbon dioxide:—

$$CH_3.CO.CH_2.CO_2H + ON.OH = CH_3.CO.CH(N.OH) + CO_2 + H_2O.$$

The isonitroso-derivatives of the higher acetones are made directly, after the same manner, from monoalkylized aceto-acetic acids and their esters (*Berichte*, 20, 531):—



$$CH_3.CO.CH\Big\langle\begin{matrix}R\\CO_2H\end{matrix} + NO.OH = CH._3CO.C\Big\langle\begin{matrix}R\\N.OH\end{matrix} + CO_2 + H_2O.$$

The dialkylic aceto-acetic acids are not reactive (*Berichte*, 15, 3067).

The isonitrosoketones are the direct product of the action of amyl nitrite, in presence of sodium ethylate or hydrochloric acid, upon the ketones. At times sodium ethylate and again hydrochloric acid gives the best yield (*Berichte*, 20, 2194; 22, 526):—

$$CH_3.CO.CH_3 + NO.O.C_5H_{11} = CH_3.CO.CH(N.OH) + C_5H_{11}.OH.$$

An excess of amyl nitrite decomposes the isonitroso-compound. The isonitroso-group is replaced by oxygen and α-diketone compounds are produced at the same time (*Berichte*, 22, 527).

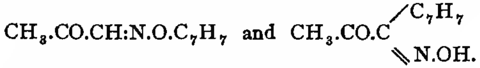
Isonitrosoketones are also produced by the action of nitrogen trioxide upon the ketones (*Berichte*, 20, 639).

The isonitroso-acetones are colorless, crystalline bodies, readily soluble in alcohol, ether and chloroform; but, as a general thing, they dissolve with difficulty in water. They impart an intense yellow color to their alkaline solutions, and with phenol and sulphuric acid yield a yellow coloration, but not the nitroso-reaction (see p. 107). When boiled with concentrated hydrochloric acid they lose hydroxylamine.

The isonitroso-group of the isonitroso-ketones can be split off and replaced by oxygen. The result will be diketo-compounds, CO.CO. This transformation may be effected by the action of sodium bisulphite, and subsequent boiling of the resulting imidosulphonic acids with dilute acids (*Berichte*, 20, 3162). The same effect is obtained by directly boiling the isonitrosoketones with dilute sulphuric acid (*Berichte*, 20, 3213). Nitrous acid sometimes produces the decomposition even more readily (*Berichte*, 22, 532).

Isonitroso-acetone, $CH_3.CO.CH(N.OH)$, is very readily soluble in water; crystallizes in silvery, glistening tablets or prisms; fuses at 65°, and decomposes at higher temperatures, but may be volatilized in a current of steam.

By the action of sodium alcoholate upon benzylchloride we get the benzyl-ether, which is isomeric with benzyl-isonitroso-acetone, obtained from benzyl-aceto acetic acid:—



$$CH_3.CO.CH{:}N.O.C_7H_7 \quad \text{and} \quad CH_3.CO.C\begin{matrix}\diagup C_7H_7\\ \diagdown N.OH.\end{matrix}$$

Isonitrosoacetone-benzyl Ether. Benzyl-isonitrosoacetone.

This is proof sufficient of the presence of the oximid-group N.OH in the isonitroso compounds (*Berichte*, 15, 3073). For the salts of the isonitrosoketones consult *Berichte*, 16, 835.

Dehydrating agents, like acetic anhydride, convert the isonitrosoketones into acidylcyanides (*Berichte*, 20, 2196).

When the isonitroso-acetones are reduced with tin and hydrochloric acid they yield peculiar bases, called *ketines* ($C_6H_8N_2$, ketine, $C_8H_{12}N_2$, dimethyl ketine). Phenylhydrazine (2 mols.) converts the isonitrosoketones into *osazones*, *e. g.*, acetone-osazone, $CH_3.C(N_2H.C_6H_5).CH(N_2H.C_6H_5)$.

Any further action of hydroxylamine (or its HCl salt, *Berichte*, 16, 182) upon isonitroso-acetone (or upon α-dichloracetone, $CH_3.CO.CHCl_2$) leads to a replacement of the ketone oxygen and the formation of

Acetoximic Acid, $CH_3.C(N.OH).CH(N.OH)$, or **Methylglyoxime**, a derivative of glyoxime, $CH(N.OH).CH(N.OH)$, (see p. 202) obtained from glyoxal, CHO.CHO. The *dialkyl-glyoximes*, like $CH_3.C(N.OH).C(N.OH).CH_3$, dimethylglyoxime, are similarly derived from the higher isonitroso-ketones. The glyoximes are solid, crystalline bodies, which dissolve with difficulty in water, and sublime without decomposition. *Methyl glyoxime* melts at 153°; *methyl-ethyl glyoxime* at 170°. Glyoxime and methyl glyoxime show an acid reaction, and dissolve in alkalies without imparting color, because the hydrogen of the CH-group is replaced. The dialkylic glyoximes, on the other hand, are insoluble in alkalies and do not yield salts (*Berichte*, 16, 180, 506, and 2185).

Di-isonitroso-acetone, $CH(N.OH).CO.CH(N.OH)$, is formed when nitrous acid acts upon acetone-dicarboxylic acid. A crystalline compound, melting at 144°. The acid solution rapidly decomposes on heating. It forms crystalline, yellow salts with alkalies (*Berichte*, 19, 2465).

Hydroxylamine converts this compound into *Tri-isonitroso-propane*, $CH(N.OH).C(N.OH).CH(N.OH)$. This crystallizes from water and alcohol in colorless needles, melting at 171° (*Berichte*, 21, 2989).

For the compounds of acetone and isonitroso-acetone with phenylhydrazine see the latter and *Berichte*, 11, 2995; 22, 528.

Condensation Products.—By the action of dehydrating agents (H_2SO_4, burnt lime, zinc chloride, hydrochloric acid) and sodium, acetone (like aldehyde, p. 195) loses a molecule of water, and condenses to complex molecules. Mesityl oxide, phorone and mesitylene are produced in this way:—

$$2C_3H_6O = \underset{\text{Mesityl Oxide.}}{C_6H_{10}O} + H_2O$$

$$3C_3H_6O = \underset{\text{Phorone.}}{C_9H_{14}O} + 2H_2O.$$

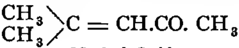
To prepare mesityl oxide and phorone, saturate acetone with HCl and let stand for some time, then treat the product with aqueous potash. On diluting with water an oily liquid separates, consisting of mesityl oxide and phorone, which are separated by fractional distillation (*Annalen*, 180, 4).

Mesityl Oxide, $C_6H_{10}O$, is a mobile liquid, smelling like peppermint and boiling at 130°. It acts like acetone; it takes on hydrogen, combines with sodium bisulphite and forms a *chloride*, $C_6H_{10}Cl_2$, with PCl_6. When boiled with dilute sulphuric or hydrochloric acid mesityl oxide decomposes into two molecules of acetone. It combines directly with Br_2 and HI.

Mesitonic or dimethyl-lævulinic acid, $C_7H_{12}O_3$, is a derivative of mesityl oxide (*Berichte*, 21, Ref. 643).

Phorone, $C_9H_{14}O$, crystallizes in large, yellow prisms, melting at 28° and boiling at 196°. Boiled with dilute sulphuric acid it breaks up into 3 molecules of acetone (mesityl oxide appears as an intermediate product). With bromine it forms a tetrabromide, fusing at 86°.

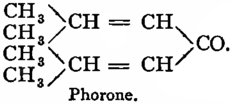
Acetone condenses to mesityl oxide and phorone in the same manner that acetaldehyde becomes crotonaldehyde (p. 194). Their structure probably agrees with the formulas (compare *Berichte*, 14, 253):—



$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C = CH.CO.CH_3$$

Mesityl Oxide.

and



$$\begin{matrix}\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CH = CH\\ \begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CH = CH\end{matrix}\!\!>CO.$$

Phorone.

Both mesityl oxide and phorone unite with hydroxylamine, yielding corresponding acetoximes (*Berichte*, 16, 494).

Mesitylene, C_9H_{12}, is produced when acetone is distilled with concentrated sulphuric acid:—

$$3C_3H_6O = C_9H_{12} + 3H_2O.$$

This is a derivative of benzene (see this). It is also produced from mesityl oxide and phorone, through the action of sulphuric acid, but if phorone be heated with P_2O_5, pseudo-cumene is obtained. Other ketones, when acted upon with sulphuric acid, also yield analogous benzene derivatives.

Acetone Bases.—When ammonia acts on acetone a condensation of two and three molecules occurs, giving rise to the bases: **Diacetonamine** and **Triacetonamine**:—

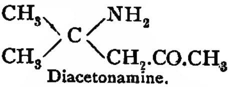
$$2C_3H_6O + NH_3 = \underset{\text{Diacetonamine.}}{C_6H_{13}NO} + H_2O.$$

$$3C_3H_6O + NH_3 = \underset{\text{Triacetonamine.}}{C_9H_{17}NO} + 2H_2O.$$

Diacetonamine is a colorless liquid, not very soluble in water. When distilled it decomposes into mesityl oxide and NH_3; conversely mesityl oxide and NH_3 combine to form diacetonamine. It acts strongly alkaline and is an amide base, forming crystalline salts with one equivalent of acid. If potassium nitrite be allowed to act on the HCl-salt *diacetone alcohol*, $(CH_3)_2C(OH).CH_2.CO.CH_3$, results; this loses water and becomes mesityl oxide.

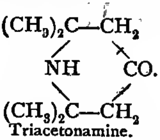
Triacetonamine crystallizes in anhydrous needles, melting at 39.6°. With one molecule of water it forms large quadratic plates, fusing at 58°. It is an imide base (p. 167) with feeble alkaline reaction; potassium nitrite converts its HCl salt into the nitroso-amine compound, $C_9H_{16}(NO)NO$, which fuses at 73° and passes into phorone when boiled with caustic soda. Hydrochloric acid regenerates triacetonamine from the nitroso-derivative.

Diacetonamine and triacetonamine are intimately related to mesityl oxide and phorone (p. 208); their structure probably corresponds to the formulas :—



Diacetonamine.

and



Triacetonamine.

By the oxidation of diacetonamine with a chromic acid mixture (p. 203) we get amido-isobutyric acid, $(CH_3)_2C(NH_2).CO_2H$, and amido-isovaleric acid, $(CH_3)_2.C(NH_2).CH_2.CO_2H$. By the addition of 2H to triacetonamine, converting the CO group into CH.OH, there results an *alkamine*, $C_9H_{19}NO$, which may be viewed as tetramethyl oxypiperidine. By the abstraction of water from this the base $C_9H_{17}N$, triacetonine, results. This approaches tropidine, $C_8H_{13}N$, very closely (*Berichte*, 16, 2236; 17, 1788).

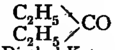
ACETONE HOMOLOGUES.

Methyl-ethyl Ketone, $\begin{matrix}CH_3\\C_2H_5\end{matrix}\rangle CO = C_4H_8O$, is formed :—

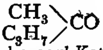
1. By oxidation of secondary butyl alcohol (p. 129).
2. By action of zinc ethide on acetyl chloride or zinc methyl upon propionyl chloride.
3. By distillation of a mixture of calcium propionate and acetate.
4. By oxidation of methyl-ethyl oxyacetic acid and from methyl aceto-acetic ester (see this).

Methyl-ethyl ketone is an agreeably smelling liquid, having a specific gravity of 0.812 at 13°, and boiling at 81°. It combines with the primary sulphites. When oxidized with chromic acid it yields two molecules of acetic acid. Its acetoxime, $CH_3.C(N.OH).C_2H_5$ (p. 205), is liquid and boils at 153°. The iso-nitroso compound, $CH_3.CO.C(N.OH).CH_3$, *isonitroso-methyl acetone*, crystallizes in pearly tables, melting at 74°, and boiling at 185°. It is converted into diacetyl, $CH_3.CO.CO.CH_3$, by the replacement of the N.OH-group. Dimethyl glyoxime, $CH_3.C(N.OH).C(N.OH).CH_3$ (p. 207) consists of colorless crystals, which melt on rapid heating.

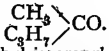
Ketones, $C_5H_{10}O$:—



Diethyl Ketone.
B. P. 101°.



Methyl-propyl Ketone.
B. P. 103°.

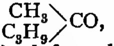


Methyl-isopropyl Ketone.
B. P. 96°.

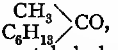
These are produced according to the methods generally employed for making the ketones. When boiled with a chromic-acid mixture, they decompose according to the rules of oxidation (p. 203), and also otherwise exhibit all the usual ketone reactions.

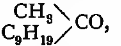
Diethyl Ketone, called **Propione**, because obtained by the distillation of calcium propionate, is obtained from carbon monoxide and potassium ethylate (p. 187). It is distinguished from the two methyl propyl ketones by not yielding compounds with the primary alkaline sulphites. Amyl nitrite converts it into isonitroso-diethyl-ketone, $CH_3.CH_2.CO.C(N.OH).CH_3$ (*Berichte*, 22, 528).

Mention may here be made of the following higher ketones :—

Methyl-tertiary Butyl Ketone, $C_6H_{12}O =$  $\begin{matrix}CH_3\\C_3H_9\end{matrix}\!\!>\!CO$, with the tertiary butyl group $(CH_3)_3C$, called **Pinacoline**, is obtained from the hexylene glycol termed pinacone, on warming with hydrochloric or dilute sulphuric acid (p. 202); also by the action of zinc methyl on trimethyl acetyl chloride. It boils at 106°. Its specific gravity at 0° is 0.823. When oxidized with chromic acid it decomposes into acetic and trimethyl acetic acids. Nascent hydrogen converts it into pinacolyl alcohol (p. 129).

Dipropyl Ketone, $C_7H_{14}O = (C_3H_7)_2CO$, **Butyrone**, is the principal product of the distillation of calcium butyrate. It boils at 144°, and at 20° has a specific gravity equal to 0.8200. A chromic acid mixture changes it to butyric and propionic acids.

Methyl Hexyl Ketone,  $\begin{matrix}CH_3\\C_6H_{13}\end{matrix}\!\!>\!CO$, **Methyl œnanthol**, is formed by the oxidation of the corresponding octyl alcohol, and the distillation of calcium œnanthylate and acetate. It boils at 171°; sp. gr. 0.818. It yields acetic and caproic acids when oxidized.

Methyl-nonyl Ketone, $C_{11}H_{22}O =$  $\begin{matrix}CH_3\\C_9H_{19}\end{matrix}\!\!>\!CO$, is the chief constituent of oil of rue (from *Ruta graveolens*); it may be extracted from this by shaking with primary sodium sulphite. It is produced in the distillation of calcium caprate with calcium acetate. It is a bluish, fluorescent oil, which on cooling solidifies to plates, melting at + 13°, and boiling at 225°. When oxidized it yields acetic and pelargonic $(C_9H_{18}O_2)$ acids.

The following additional ketones have been obtained by distilling the barium salts of fatty acids with barium acetate (*Berichte*, 15, 1710):—

			Melting Points of the Ketones.
$C_{12}H_{24}O = C_{10}H_{21}.CO.CH_3$	from	undecylic acid.	21°
$C_{13}H_{26}O = C_{11}H_{23}.CO.CH_3$	"	lauric "	28°
$C_{14}H_{28}O = C_{12}H_{25}.CO.CH_3$	"	tridecylic "	34°
$C_{15}H_{30}O = C_{13}H_{27}.CO.CH_3$	"	myristic "	39°
$C_{16}H_{32}O = C_{14}H_{29}.CO.CH_3$	"	pentadecatoic acid.	43°
$C_{17}H_{34}O = C_{15}H_{31}.CO.CH_3$	"	palmitic acid.	48°
$C_{18}H_{36}O = C_{18}H_{33}.CO.CH_3$	"	margaric "	52°
$C_{18}H_{38}O = C_{17}H_{35}.CO.CH_3$	"	stearic "	55.5°

When the salts of the higher fatty acids are distilled alone (p. 187) the simple ketones (with two similar alkyls) result:—

				Melting Points of the Ketones.
$C_{11}H_{22}O = (C_5H_{11})_2CO$	caprone	from	caproic acid.	14.6°
$C_{13}H_{26}O = (C_6H_{13})_2CO$	œnanthone	"	œnanthylic acid.	30°
$C_{15}H_{30}O = (C_7H_{15})_2CO$	caprylone	"	caprylic "	40°
$C_{17}H_{34}O = (C_8H_{17})_2CO$	nonone	"	nonoic "	58°
$C_{23}H_{46}O = (C_{11}H_{23})_2CO$	laurone	"	lauric "	69°
$C_{27}H_{54}O = (C_{13}H_{27})_2CO$	myristone	"	myristic "	76°
$C_{31}H_{62}O = (C_{15}H_{31})_2CO$	palmitone	"	palmitic "	83°
$C_{35}H_{70}O = (C_{17}H_{35})_2CO$	stearone	"	stearic "	88°

The corresponding paraffins are obtained when these ketones are reduced (see p. 76).

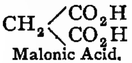
MONOBASIC ACIDS.

The organic acids are characterized by the atomic group, CO.OH, called *carboxyl.* The hydrogen of this can be replaced by metals, forming salts (see p. 115). These organic acids may be compared to the analogously constituted sulphonic acids, containing the sulpho-group, $SO_2.OH$.

The number of carboxyl groups present in them determines their basicity, and distinguishes them as mono-, di-, tri-basic, etc., or as mono-, di- and tri-carboxylic acids:—

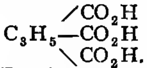
$CH_3.CO_2H$

Acetic Acid.
Monobasic.



$$CH_2\begin{cases}CO_2H\\CO_2H\end{cases}$$

Malonic Acid.
Dibasic.



$$C_3H_5\begin{cases}CO_2H\\CO_2H\\CO_2H.\end{cases}$$

Tricarballylic Acid.
Tribasic.

We can view the monobasic *saturated* acids as combinations of the carboxyl group with alcohol radicals; they are ordinarily termed *fatty acids.* The *unsaturated* acids of the acrylic acid and propiolic acid series, corresponding to the unsaturated alcohols, are derived from the fatty acids by the exit of two and four hydrogen atoms.

The most important and general methods of obtaining the monobasic acids are:—

1. Oxidation of the primary alcohols and aldehydes:—

$$\underset{\text{Ethyl Alcohol.}}{CH_3.CH_2.OH} + O_2 = \underset{\text{Acetic Acid.}}{CH_3.CO.OH} + H_2O,$$

$$\underset{\text{Aldehyde.}}{CH_3.COH} + O = \underset{\text{Acetic Acid.}}{CH_3.CO.OH.}$$

2. The transformation of the cyanides of the alcohol radicals (the so-called nitriles), by heating them with alkalies or dilute mineral acids. The cyanogen group changes to the carboxyl group, while the nitrogen separates as ammonia:—

$$CH_3.CN + 2H_2O + HCl = CH_3.CO_2H + NH_4Cl \text{ and}$$
$$CH_3.CN + H_2O + KOH = CH_3.CO_2K + NH_3.$$

The change of the nitriles to acids is, in many instances, most advantageously executed by digesting the former with sulphuric acid (diluted with an equal volume of water); the fatty acid will then appear as an oil upon the top of the solution. (*Berichte,* 10, 262.)

To convert the nitriles directly into esters of the acids, dissolve them in alcohol, and conduct HCl into this solution, or warm the same with sulphuric acid. (*Berichte,* 9, 1590.)

3. Action of carbon dioxide upon sodium alkyls (see p. 178):—

$$C_2H_5Na + CO_2 = C_2H_5.CO_2Na.$$

4. Action of carbon monoxide upon the sodium alcoholates heated to 160°–200°.

$$\underset{\text{Sodium Ethylate.}}{C_2H_5.ONa} + CO = \underset{\text{Sodium Propionate.}}{C_2H_5.CO_2Na.}$$

Formic acid results when the caustic alkalies are employed :—

$$HONa + CO = H.CO_2Na.$$

Sodium Formate.

Usually, the reaction is very incomplete, and is often accompanied by secondary reactions, resulting in the formation of higher acids. (*Annalen*, 202, 294.)

5. By the action of phosgene gas upon the zinc alkyls. At first acid chlorides are formed, but they subsequently yield acids with water :—

$$Zn(CH_3)_2 + 2COCl_2 = 2CH_3.COCl + ZnCl_2, \text{ and}$$

Acetyl Chloride.

$$CH_3.CO.Cl + H_2O = CH_3.CO.OH + HCl.$$

Acetic Acid.

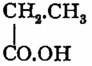
6. The following is a very interesting and a commonly applied method for the synthesis of the fatty acids. By the action of sodium upon acetic esters, the so-called aceto-acetic esters are produced, in which, by the aid of sodium and alkyl iodides, one and two hydrogen atoms can be replaced by alkyls (R) (see aceto-acetic esters) :—

$$CH_3.CO.CH_2.CO.O.C_2H_5 \text{ yields } \left\{ \begin{array}{l} CH_3.CO.CH(R).CO.O.C_2H_5, \text{ and} \\ CH_3.CO.C(R_2).CO.O.C_2H_5. \end{array} \right.$$

Sodium alcoholate decomposes these alkylic esters (or alkyl ketonic acids) in such a manner, that the group $CH_3.CO$ splits off and the fatty acid esters are produced, but are at once saponified, yielding salts :—

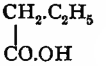
$$\begin{array}{lcl} CH_3.CO.CH(R).CO.O.C_2H_5 & \text{yields} & CH_2(R).CO.OH \\ CH_3.CO.C(R_2).CO.O.C_2H_5 & \text{"} & CH(R_2).CO.OH. \end{array}$$

We may regard the acids thus obtained as the direct derivatives of acetic acid, $CH_3.CO.OH$, in which one and two hydrogen atoms of the CH_3 group are replaced by alkyls; hence, the designations, methyl and dimethyl acetic acid, etc. :—



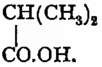
$$\begin{array}{l} CH_2.CH_3 \\ | \\ CO.OH \end{array}$$

Methyl Acetic Acid
or Propionic Acid.



$$\begin{array}{l} CH_2.C_2H_5 \\ | \\ CO.OH \end{array}$$

Ethyl Acetic Acid
or Butyric Acid.

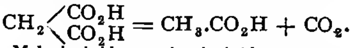


$$\begin{array}{l} CH(CH_3)_2 \\ | \\ CO.OH. \end{array}$$

Dimethyl Acetic Acid
or Isobutyric Acid.

Very many fatty acids have been prepared in the above way (first by Frankland and Duppa).

7. From the dicarboxylic acids, in which the two carboxyl groups are in union with the same carbon atom. On the application of heat, these sustain a loss of carbon dioxide :—



$$CH_2 \left\langle \begin{array}{l} CO_2H \\ CO_2H \end{array} \right. = CH_3.CO_2H + CO_2.$$

Malonic Acid. Acetic Acid.

In malonic acid, as in aceto-acetic acid (its esters, see above), the hydrogen atoms of the group CH_2 may be replaced by alkyls; the resulting alkylic malonic acids, when heated, sustain a loss of carbon dioxide, and form alkylic acetic acids. (*Berichte*, 13, 595.)

The isomerisms of the monobasic acids are influenced by the isomerisms of the hydrocarbon radicals, to which the carboxyl group is attached. There are no possible isomerides of the first three members of the series $C_nH_{2n}O_2$:—

HCO_2H	$CH_3.CO_2H$	$C_2H_5.CO_2H.$
Formic Acid.	Acetic Acid.	Propionic Acid.

Two structural cases are possible for the fourth member, $C_4H_8O_2$:

$CH_3.CH_2.CH_2.CO_2H$ and $(CH_3)_2.CH.CO_2H.$
Butyric Acid. Isobutyric Acid.

Four isomerides are possible with the fifth member, $C_5H_{10}O_2 = C_4H_9.CO_2H$, inasmuch as there are four butyl, C_4H_9, groups, etc.

The hydrogen of carboxyl replaced by metals yields salts, and when replaced by alkyls, compound ethers or esters are formed (see p. 146).

$$CH_3.CO.OH + KOH = \underset{\text{Potassium Acetate.}}{CH_3.CO_2K} + H_2O.$$

$$CH_3.CO.OH + C_2H_5.OH = \underset{\text{Ethyl Acetic Ester.}}{CH_3.CO.O.C_2H_5} + H_2O.$$

The residues combined in the acids with hydrogen are termed *acid radicals*:—

$CH_3.CO—$	$CH_3.CH_2.CO—$	$CH_3.CH_2.CH_2.CO—$
Acetyl.	Propionyl.	Butyryl.

These are capable of entering various combinations. Their halogen derivatives, or the *haloid anhydrides* of the acids, like

$CH_3.CO.Cl$	$CH_3.CH_2.CO.Cl.$
Acetyl Chloride.	Propionyl Chloride.

are produced when the halogen derivatives of phosphorus act upon the acids or their salts (p. 92):—

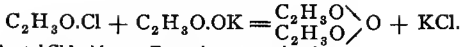
$$CH_3.CO.OH + PCl_5 = CH_3.CO.Cl + PCl_3O + HCl.$$

The aldehydes are the hydrides of these acid radicals, and the ketones their compounds with alcohol radicals:—

$CH_3.CO.H$	$CH_3.CO\,CH_3.$
Acetaldehyde.	Acetone.

The conversion of the acids into aldehydes and ketones has already received attention (pp. 188 and 200).

When an atom of oxygen unites two acid radicals we obtain oxides of the latter, or the *acid anhydrides*:—



$$C_2H_3O.Cl + C_2H_3O.OK = \left.\begin{matrix}C_2H_3O\\C_2H_3O\end{matrix}\right>O + KCl.$$

Acetyl Chloride. Potassium Acetate. Acetic Anhydride.

The *amides* of the acids appear by the union of the acid radicals with the amido group:—

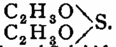
$$C_2H_3O.Cl + NH_3 = C_2H_3O.NH_2 + HCl.$$

Acetamide.

Sulphur Compounds, corresponding to the acids and their anhydrides, exist:—

$$C_2H_3O.SH$$

Thioacetic Acid.



$$\left.\begin{matrix}C_2H_3O\\C_2H_3O\end{matrix}\right>S.$$

Acetyl Sulphide.

Furthermore, *substituted* acids are obtained by the direct substitution of halogens for the hydrogen of the alkyls present in the acids:—

$$CH_2Cl.CO_2H \qquad CCl_3.CO_3H.$$

Monochlor-acetic Acid. Trichlor-acetic Acid.

The *fluorine* derivatives (their esters) appear to form when HFl acts upon the esters of the diazo-fatty acids (see these): $CN_2HCO_2H + HFl = CH_2Fl.CO_2H + N_2$.

The nitro-derivatives of the fatty acids are prepared by treating some of the iod acids with silver nitrite (see Nitropropionic acid), or by the action of nitric acid upon the fatty acids containing a tertiary CH-group (*Berichte*, 15, 2318).

Isonitroso-derivatives are obtained from the ketone acids by the action of hydroxylamine (p. 203).—

$$CH_3.CO.CO_2H + H_2N.OH = CH_3.C(N.OH).CO_2H + H_2O.$$

Acetyl-carboxylic Acid. α-Isonitroso-propionic Acid.

In the same manner the β-isonitroso-acids are produced from the aceto-acetic esters (and their alkyl derivatives) by means of $H_2N.OH$ and saponification with alkalies (*Berichte*, 16, 2996):—

$$CH_3.CO.CH_2.CO_2R \quad \text{yields} \quad CH_3.C(N.OH).CH_2.CO_2H.$$

Aceto-acetic Ester. β-Isonitroso-butyric Acid.

Alcoholic sodium and $NaNO_2$ acting on the monoalkylic aceto-acetic esters, produce the α-isonitroso-acids (*Berichte*, 15, 1057; 16, 2180):—

$$CH_3.CO.CHR.CO_2R \quad \text{yields} \quad R.C(N.OH).CO_2H.$$

By reduction with tin and hydrochloric acid these derivatives become amido-acids. They do not give the nitroso-reaction with phenol and sulphuric acid (p. 107).

Of the decomposition reactions of the acids those may be mentioned again which lead to the formation of hydrocarbons.

1. The distillation of the alkali salts with alkalies or lime (see p. 71):—

$$CH_3.CO_2K + KOH = CH_4 + CO_3K_2.$$

2. The electrolysis of the alkali salts in concentrated aqueous solution; hydrogen separates upon the negative pole, and carbon dioxide and the hydrocarbon upon the positive (see p. 71):—

$$2CH_3.CO_2K + H_2O = C_2H_6 + CO_3K_2 + CO_2 + H_2.$$

It may not be amiss here to direct attention to the successive reduction of the higher into lower fatty acids. It serves as an excellent mode of preparing the latter. To this end the acid is first converted into its amide, and this, by the reaction of Hofmann (p. 159) (action of Br and NaOH), is changed into the next lower amine. The further action of bromine and sodium hydroxide changes the amine into a nitrile, and the latter is then readily converted into the corresponding acid-amide; from which again by the further action of Br and NaOH the next lower amine results (*Berichte*, 19, 1433):—

$C_{14}H_{28}O_2$ Myristic Acid.	$C_{13}H_{27}.CO.NH_2$ Myristic Amide.	$C_{13}H_{27}NH_2$ Tridecylamine.
$C_{12}H_{25}CN$ Tridecyl Nitrile.	$C_{12}H_{25}.CO.NH_2$, etc. Tridecylamide.	

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1. FATTY ACIDS, $C_nH_{2n}O_2$.

Formic	Acid	CH_2O_2	=	HCO_2H
Acetic	“	$C_2H_4O_2$	=	$CH_3.CO_2H$
Propionic	“	$C_3H_6O_2$	=	$C_2H_5.CO_2H$
Butyric	“	$C_4H_8O_2$	=	$C_3H_7.CO_2H$
Valeric	“	$C_5H_{10}O_2$	=	$C_4H_9.CO_2H$
Caproic	“	$C_6H_{12}O_2$	=	$C_5H_{11}.CO_2H$
Œnanthylic	“	$C_7H_{14}O_2$	=	$C_6H_{13}.CO_2H$

Caprylic	Acid	$C_8H_{16}O_2$	+ 16° *	Pelargonic	Acid	$C_9H_{18}O_2$	+ 12°
Capric	“	$C_{10}H_{20}O_2$	31.4°	Undecylic	“	$C_{11}H_{22}O_2$	28°
Lauric	“	$C_{12}H_{24}O_2$	43.6°	Tridecylic	“	$C_{13}H_{26}O_2$	40.5°
Myristic	“	$C_{14}H_{28}O_2$	54°	Pentadecatoic	“	$C_{15}H_{30}O_2$	51°
Palmitic	“	$C_{16}H_{32}O_2$	62°	Margaric	“	$C_{17}H_{34}O_2$	60°
Stearic	“	$C_{18}H_{36}O_2$	69°	Nondecylic	“	$C_{19}H_{38}O_2$	65.5°
Arachidic	“	$C_{20}H_{40}O_2$	75°	Medullic	“	$C_{21}H_{42}O_2$	72°
Behenic	“	$C_{22}H_{44}O_2$	73°	—	“	$C_{23}H_{46}O_2$	—
Lignoceric	“	$C_{24}H_{48}O_2$	80.5°	Hyænic	“	$C_{25}H_{50}O_2$	77°

Cerotic	Acid		$C_{27}H_{54}O_2$	79°
Melissic	“		$C_{30}H_{60}O_2$	91°
Theobromic	“	(?)	$C_{64}H_{128}O_2$	72°

The acids of this series are known as the *fatty acids*, because their higher members occur in the natural fats, and the free acids (excepting the first members) resemble fats. The latter are ester-like

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* Melting points.

compounds of the fatty acids, and are chiefly esters of the trihydric glycerol. On boiling them with caustic potash or soda (saponification) alkali salts of the fatty acids are formed, and from these the mineral acids release the fatty acids.

The lower acids (with exception of the first members) are oily liquids; the higher, commencing with capric acid, are solids at ordinary temperatures. The first can be distilled without decomposition; the latter are partially decomposed, and can only be distilled without alteration in vacuo. All of them are readily volatilized with steam. Acids of like structure show an increase in their boiling temperatures of about 19° for every $+ CH_2$. It may be remarked, in reference to the melting points, that these are higher in acids of normal structure, containing an even number of carbon atoms, than in the case of those having an odd number of carbon atoms (see above). The dibasic acids exhibit the same characteristic. As the oxygen content diminishes, the specific gravities of the acids grow successively less, and the acids themselves at the same time approach the hydrocarbons. The lower members are readily soluble in water. The solubility in the latter regularly diminishes with increasing molecular weight. All are easily soluble in alcohol, and especially so in ether. Their solutions redden blue litmus. Their acidity diminishes with increasing molecular weight; this is very forcibly expressed by the diminution of the heat of neutralization, and the initial velocity in the etherification of the acids.

A mixture of the volatile acids can be separated by fractionation only with great difficulty. It is advisable to combine this with a *partial saturation*. For instance, a mixture of two acids, *e.g.*, butyric and valeric acids, is about half saturated with potash, and the aqueous solution distilled as long as the distillate continues to react acid. If enough alkali had been added to saturate the less volatile acid (in this case valeric), the more volatile compound (butyric acid) will be almost the sole constituent of the distillate. Should the contrary be the real condition, the distillate is subjected again to the same operation. The residue after distillation is a mixture of salts of both acids. This is true when the quantity of alkali was more than sufficient for the saturation of the less volatile acid (valeric). The acids are liberated from their salts by distillation with sulphuric acid, and the distillate again submitted to the process described above.

To be assured of the purity of the acids, the aqueous solution of their alkali salts is fractionally precipitated with silver nitrate. The less soluble silver salts (of the higher acids) are the first to separate out.

(1) Formic Acid, $CH_2O_2 = HCO.OH$.

Formic acid (*Acidum formicum*) is found free in ants, in stinging nettles, in shoots of the pine, in various animal secretions, and may be obtained from these substances by distilling them with water. It is produced artificially according to the usual methods (p. 211): by the oxidation of methyl alcohol; by heating hydrocyanic acid with alkalies or acids:—

$$HCN + 2H_2O = HCO.OH + NH_3;$$

and on boiling chloroform with alcoholic potash:—

$$CHCl_3 + 4KOH = HCO.OK + 3KCl + 2H_2O.$$

Worthy of mention, is the direct production of formates by the action of CO upon concentrated potash at 100°. The reaction occurs more easily if soda-lime at 200°–220° (*Berichte*, 13, 718) be employed:—

$$CO + NaOH = HCO.ONa;$$

also by letting moist carbon dioxide act upon potassium:—

$$3CO_2 + 4K + H_2O = 2HCO.OK + CO_3K_2;$$

potassium carbonate is produced at the same time.

Formates are also formed in the action of sodium amalgam upon a concentrated aqueous ammonium carbonate solution, or with the same reagent upon aqueous primary carbonates:—$CO_3KH + H_2 = HCO_2K + H_2O$; likewise on boiling zinc carbonate with caustic potash and zinc dust. In all these methods it is the nascent hydrogen which, in presence of the alkali, unites itself to carbon dioxide:—

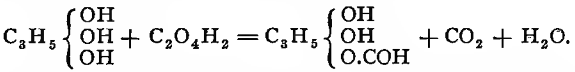
$$CO_2 + 2H + KOH = HCO.OK + H_2O.$$

The most practical method of preparing formic acid consists in heating oxalic acid:—

$$C_2O_4H_2 = HCO.OH + CO_2.$$

This decomposition is accelerated by the presence of glycerol, because free oxalic acid sublimes with partial decomposition:—

Crystallized oxalic acid ($C_2O_4H_2 + 2H_2O$) is added to moist concentrated glycerol and the whole heated to 100–110°. Carbon dioxide is evolved and formic acid distils over. As soon as CO_2 ceases generating, add more oxalic acid and heat anew, when a concentrated formic acid passes over. Continued addition of oxalic acid and the application of heat furnish a regular 56 per cent. aqueous formic acid. The mechanism of the reaction is this: on heating crystallized oxalic acid it parts with its water of crystallization and unites with the glycerol to form *glycerol formic ester* (see p. 135):—



$$C_3H_5\begin{cases}OH\\OH\\OH\end{cases} + C_2O_4H_2 = C_3H_5\begin{cases}OH\\OH\\O.COH\end{cases} + CO_2 + H_2O.$$

On further addition of oxalic acid the latter again breaks up into anhydrous acid and water, which converts the glycerol formic ester into glycerol and formic acid:—

$$C_3H_5(OH)_2.(O.CHO) + H_2O = C_3H_5(OH)_3 + CHO.OH.$$

The anhydrous oxalic acid unites anew with the regenerated glycerol to produce the formic ester. The quantities of acid and water distilling over in the latter part of the operation correspond to the equation:—

$$C_2H_4O_2 + 2H_2O = CH_2O_2 + CO_2 + 2H_2O.$$

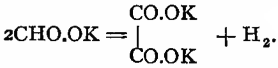
To obtain anhydrous acid, the aqueous product is boiled with PbO and the beautifully crystallized lead salt decomposed, at 100°, in a current of hydrogen sulphide. If anhydrous acid be employed in the reaction a 95–98 per cent. formic acid can be immediately obtained. Boron trioxide will completely dehydrate this (*Berichte*, 14, 1709).

Anhydrous formic acid is a mobile liquid, with a specific gravity of 1.223 at 0° and boils at 99°. It becomes crystalline at 0°, and fuses at +8.6°. It has a pungent odor (from ants) and causes blisters on the skin. It mixes in all proportions with water, alcohol and ether, and yields the hydrate $2CH_2O_2 + H_2O$, which boils at 105° and dissociates into formic acid and water. Concentrated, hot sulphuric acid decomposes formic acid into carbon monoxide and water:—$CH_2O_2 = CO + H_2O$. A temperature of 160° suffices to break up the acid into carbon dioxide and hydrogen. The same change may occur at ordinary temperatures by the action of pulverulent rhodium, iridium and ruthenium, but less readily when platinum sponge is employed.

According to its structure, HCO.OH, formic acid is also an aldehyde, as it contains the group CHO; this would account for its reducing property, its ability to precipitate silver from a hot neutral solution of silver nitrate, and mercury from mercuric nitrate, the acid itself oxidizing to carbon dioxide.

The formates, excepting the sparingly soluble lead and silver salts, are readily soluble in water.

The alkali salts deliquesce in the air; heated carefully to 250° they become oxalates:—



$$2CHO.OK = \begin{array}{l} CO.OK \\ | \\ CO.OK \end{array} + H_2.$$

By strong ignition of the resulting oxalate with an excess of alkali it decomposes with the formation of a carbonate and the liberation of hydrogen. These reactions serve for the preparation of pure hydrogen. The ammonium salt, $CHO.O.NH_4$, decomposes into hydrogen cyanide and water when heated to 180°:—

$$CHO_2.NH_4 = CNH + 2H_2O.$$

The lead salt, $(CHO_2)_2Pb$, crystallizes in brilliant needles, soluble in 36 parts of cold water. The silver salt, CHO_2Ag, is obtained by the double decomposition of the alkali salt with silver nitrate. It is precipitated in the form of white needles that rapidly blacken on exposure to light. When heated, it decomposes into silver, carbon dioxide and formic acid:—

$$2CHO_2Ag = 2Ag + CO_2 + H.CO_2H.$$

The mercury salt sustains a similar decomposition.

Monochlorformic acid, CClO.OH, is regarded as chlor-carbonic acid.

(2) Acetic Acid, $C_2H_4O_2 = CH_3.CO_2H$.

This acid (*Acidum aceticum*) is produced in the decay of many organic substances and in the dry distillation of wood, sugar, tartaric acid, and other compounds. It may be synthetically prepared:

1. By the action of carbon dioxide upon sodium methyl:—

$$CH_3.Na + CO_2 = CH_3.CO_2Na;$$

2. By heating sodium methylate with carbon monoxide to 100°:—

$$CH_3.ONa + CO = CH_3.CO_2Na;$$

3. By boiling methyl cyanide (acetonitrile) with alkalies or acids (p. 211):—

$$CH_3.CN + 2H_2O = CH_3.CO_2H + NH_3.$$

It is made on a large scale by the oxidation of ethyl alcohol, and by the distillation of wood.

(1) In the presence of platinum sponge, the oxygen of the air converts ethyl alcohol into acetic acid; this occurs, too, in the *acetic fermentation* induced by a minute organism (*Mycoderma aceti*). The process is applied technically in the manufacture of vinegar (p. 220). Dilute aqueous solutions of whiskey, wine or starch mash are mixed with vinegar and yeast, and exposed to the air at a temperature of 20–40°. To hasten the oxidation, proceed as follows: Large, wooden tubs are filled with shavings previously moistened with vinegar, then the diluted (10 per cent.) alcoholic solutions are poured upon these. The lower part of the tub is provided with a sieve-like bottom, and all about it are holes permitting the entrance of air to the interior. The liquid collecting on the bottom is run through the same process two or three times, to insure the conversion of all the alcohol into acetic acid. It is very evident that this process is based on accelerated oxidation, due to the increased exposure of the liquid surface to the air.

Pasteur contends that the presence of porous substances (wood shavings) is not required in the vinegar manufacture, all that is necessary being the exposure of the alcoholic fluid, mixed with *Mycoderma aceti*, to the air. (French or Orleans Method.)

(2) Considerable quantities of acetic acid are also obtained by the dry distillation of wood in cast-iron retorts. The aqueous distillate, consisting of acetic acid, wood spirit, acetone, and empyreumatic oils, is neutralized with soda, evaporated to dryness, and the residual sodium salt heated 230°–250°. In this manner, the greater portion of the various organic admixtures is destroyed, sodium acetate remaining unaltered. The salt purified in this way is distilled with sulphuric acid when acetic acid is set free and purified by further distillation over potassium chromate.

Anhydrous acetic acid at low temperatures consists of a leafy, crystalline mass, fusing at 16.7°, and forming at the same time a penetrating, acid-smelling liquid, of specific gravity 1.0514 at 20°. It boils at 118°, and mixes with water in all proportions. In this case, a contraction first ensues, consequently the specific gravity increases until the composition of the solution corresponds to the hydrate, $C_2H_4O_2 + H_2O$ ($= CH_3.C(OH)_3$); the specific gravity then equals 1.0754 at 15°. On further dilution, the specific gravity becomes less, until a 50 per cent. solution possesses about the same specific gravity as anhydrous acetic acid. Ordinary vinegar contains about 5–15 per cent. acetic acid. Pure acetic acid should not decolorize a drop of potassium permanganate.

Acetates. The acid combines with one equivalent of the bases, forming readily soluble, crystalline salts. It also yields basic salts with lead and copper; these dissolve with difficulty in water. The alkali salts have the additional property of combining with a molecule of acetic acid, yielding *acid* salts, $C_2H_3KO_2 + C_2H_4O_2$. In this respect, acetic acid behaves like a dibasic acid. The fact that it furnishes only neutral esters proves it, however, to be only monobasic. The existence of acid salts points to a condensation of two molecules of the acid, analogous to that occurring with the aldehydes.

Potassium Acetate, $C_2H_3KO_2$, deliquesces in the air, and dissolves readily in alcohol. Carbon dioxide will set free acetic acid and precipitate potassium carbonate in such an alcoholic solution; but in an aqueous solution, acetic acid will displace carbon dioxide from the carbonates. On adding acetic acid to neutral potassium acetate, an *acid* salt, $C_2H_3KO_2.C_2H_4O_2$, crystallizes out on evaporation; this consists of pearly leaflets. It fuses at 148°, and at 200° decomposes into the neutral salt and acetic acid.

Sodium Acetate, $C_2H_3NaO_2 + 3H_2O$, crystallizes in large, rhombic prisms, soluble in 2.8 parts water at medium temperatures. The crystals effloresce on exposure, and lose all their water. When heated, the anhydrous salt remains unchanged at 310°.

Ammonium Acetate, $C_2H_3(NH_4)O_2$, is obtained as a crystalline mass on saturating acetic acid with ammonia. When the aqueous solution is evaporated, the salt decomposes into acetic acid and ammonia. Heat applied to the dry salt converts it into water and acetamide, $C_2H_3.O.NH_2$.

Ferrous Acetate, $(C_2H_3O_2)_2Fe$, is produced on dissolving iron in acetic acid; it consists of green colored, readily soluble prisms. The aqueous solution oxidizes in the air to basic ferric acetate. Neutral ferric acetate, $(C_2H_3O_2)_6Fe_2$, is not crystallizable, and dissolves in water with a deep, reddish-brown color. On boiling, ferric oxide is precipitated in the form of basic acetate. The same may be said in regard to aluminium acetate.

Neutral Lead Acetate, $(C_2H_3O_2)_2Pb + 3H_2O$, is obtained by dissolving litharge in acetic acid. The salt forms brilliant four-sided prisms, which effloresce on exposure. It possesses a sweet taste (hence, called *sugar of lead*), and is poisonous. When heated, it melts in its water of crystallization, loses all of the latter at 100°, and at higher temperatures passes into acetone, CO_2, and lead oxide. If an aqueous solution of sugar of lead be boiled with litharge, *basic lead salts* of varying lead content are produced. Their alkaline solutions find application under the designation—*lead vinegar.* Solutions of basic lead acetates absorb carbon dioxide from the air and deposit *basic carbonates* of lead—white lead.

Neutral Copper Acetate, $(C_2H_3O_2)_2Cu + H_2O$, is obtained by the solution of cupric oxide in acetic acid, and crystallizes in dark-green rhombic prisms. It is easily soluble in water. *Basic copper* salts occur in trade under the title of *verdi-*

gris. They are obtained by dissolving copper strips in acetic acid in presence of air. The double salt of acetate and arsenite of copper is the so-called *Schweinfurt Green—mitis green.*

Silver Acetate, $C_2H_3O_2Ag$, separates in brilliant needles or leaflets when concentrated acetate solutions and silver nitrate are mixed. The salt is soluble in 98 parts water at 14° C.

SUBSTITUTION PRODUCTS OF ACETIC ACID.

The three hydrogen atoms of the methyl group in acetic acid can be replaced by halogens. The chlorine derivatives result by the action of chlorine in the sunlight upon acetic acid, or if chlorine be conducted into a boiling aqueous solution of the acid containing iodine (compare p. 91). It is more practicable to chlorinate acetyl chloride, $C_2H_3O.Cl$, and convert the product into the acids by means of water. In this way a mixture of the mono-, di-, and tri-substituted acids is always formed. They may be separated by fractional distillation. They are more powerful acids than acetic. The monohalogen fatty acids can be obtained from their corresponding oxy-fatty acids by the action of the haloid acids: $CH_2OH.CO_2H + HBr = CH_2Br.CO_2H + H_2O$; as well as from the diazo-fatty acids (see these).

Monochloracetic Acid, $CH_2Cl.CO_2H$ (Preparation, *Berichte*, 17, 1286), crystallizes in rhombic prisms or plates, fusing at 62°, and boiling at 185°–187°. The silver salt, $C_2H_2ClO_2Ag$, crystallizes in pearly, glistening scales, and at 70° decomposes into AgCl and glycolide. The *ethyl ester*, $C_2H_2ClO_2.C_2H_5$, obtained by conducting HCl into a mixture of the acid and absolute alcohol, boils at 143.5°.

When monochloracetic acid is heated with alkalies or silver oxide, the chlorine is replaced by the hydroxyl group and we get glycollic acid ($C_2H_3(OH)O_2$). Amido-acetic acid, $CH_2(NH_2).CO_2H$, or glycocoll, results when the monochloracid is digested with ammonia.

Dichloracetic Acid, $CHCl_2.CO_2H$, is produced when chloral is heated with CNK and some water:—

$$CCl_3.CHO + H_2O + CNK = CHCl_2.CO_2H + KCl + CNH,$$

and by the action of alkalies upon trichloracetic acid (*Berichte*, 18, 757). It boils from 190°–191°, and solidifies below 0°. The free acid is best obtained by heating its potassium salt (prepared from the ethyl ester) in a current of HCl gas.

The *ethyl ester*, $C_2HCl_2O.O.C_2H_5$, is prepared by the action of potassium cyanide and alcohol upon chloral. (For the mechanism of this peculiar reaction, see *Berichte*, 10, 2120.) It is a heavy liquid, boiling from 156°–157°. Alcoholic potash decomposes it immediately into potassium dichloracetate and alcohol. When the acid is boiled with aqueous potash, it breaks up into oxalic and acetic acids. The salts of the di-chlor acid reduce silver solutions, forming at first glyoxylic acid (*Berichte*, 18, 227).

Trichloracetic Acid, $CCl_3.CO_2H$, is made by letting chlorine act in the sunlight upon tetrachlorethylene, C_2Cl_4. It is best obtained by the oxidation of chloral with fuming nitric acid, chromic acid, potassium permanganate, or potassium chlorate (*Berichte*, 18, 3336):—

$$CCl_3.COH + O = CCl_3.CO_2H.$$

It consists of rhombic crystals, which deliquesce, melt at 52°, and boil at 195°. It yields easily soluble, crystalline salts with bases, but on evaporation they are soon broken up. The *ethyl ester*, $C_2Cl_3O.O.C_2H_5$, boils at 164°.

When the acid is heated with ammonia or alkalies it yields $CHCl_3$ and carbon dioxide: $CCl_3.CO_2H = CCl_3H + CO_2$. Sodium alcoholate changes it into potassium carbonate and formate, and potassium chloride.

Nascent hydrogen (sodium amalgam) reconverts the substituted acetic acids into the original acetic acid.

The bromine substitution acids result when anhydrous acetic acid is heated in sealed tubes along with bromine.

The bromination is more readily effected (also in the case of the homologous acids) in the presence of amorphous phosphorus (Hill). Then, under certain circumstances, the reaction proceeds without pressure, and the monosubstituted acids are the sole products (Volhard) (*Berichte*, 21, Ref. 5; 21, 1725 and 1904).

Monobromacetic Acid, $C_2H_3BrO_2$ (Preparation, see *Berichte*, 16, 2502), crystallizes in deliquescent rhombohedra, and boils at 208°. Its *ethyl ester*, $C_2H_2BrO_2.C_2H_5$, is a liquid which boils at 159°, and suffers a slight decomposition at the same time.

Dibromacetic Acid, $C_2H_2Br_2O_2$, is a crystalline mass, melting at 54–56°, and boiling from 232–235°. Its salts are very unstable. The *Ethyl ester*, $C_2HBr_2O.O.C_2H_5$, like that of the dichloracid, may be prepared from bromal with CNK and alcohol. It boils at 192–194°.

Tribromacetic Acid, $C_2HBr_3O_2$, made from tribromacetyl bromide, $CBr_3.COBr$, and by the oxidation of bromal with nitric acid, consists of table-like crystals, permanent in the air. It melts at 135°, and boils at 245°.

The iodine substitution acids (their esters) are obtained from the chlor- and brom-acid esters when the latter are heated with potassium iodide (p. 95). They are also produced on boiling acetic acid anhydride with iodine and iodic acid (p. 91).

Moniodacetic Acid, $C_2H_3IO_2$, crystallizes in colorless plates, which melt at 82°, and decompose when more strongly heated. Its salts are unstable. The *ethyl ester* boils at 178–180°. When heated with HI it passes into acetic acid (p. 91): $CH_2I.CO_2 + HI = CH_3.CO_2H + I_2$.

Di-iodacetic Acid, $CHI_2.CO_2H$. Its ethyl ester, first prepared from dibromacetic acid ester and KI, may also be made by allowing iodine to act upon diazo-acetic ester (see this). It is a heavy, bright-yellow colored oil. It is volatile with steam, decomposes on heating, and when exposed to the air liberates iodine rapidly.

Ethyl Nitroacetic Ester, $CH_2(NO_2).CO_2.C_2H_5$, is produced in the action of silver nitrite upon bromacetic ester, and boils at 151–152° with scarcely any decomposition. By reduction with tin and hydrochloric acid it yields amido-acetic acid. The free nitro-acetic acid at once decomposes into nitromethane, $CH_3.(NO_2)$, and CO_2.

Ethyl Isonitroso-acetic Ester, $CH(N.OH).CO_2.(C_2H_5)$, or oximido-acetic ester (p. 205), is produced by the action of nitric acid upon the aceto-acetic ester. It is a yellow oil, which suffers decomposition when distilled (*Annalen*, 222, 48).

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3. **Propionic Acid**, $C_3H_6O_2 = CH_3.CH_2.CO_2H$, may be prepared by the methods in general use in making fatty acids, and by the oxidation of normal propyl alcohol with chromic acid, or from

ethyl cyanide, $C_2H_5.CN$ (propio-nitrile) by the action of sulphuric acid (p. 211). Especially noteworthy is its formation from acrylic acid, $C_3H_4O_2$, through the agency of nascent hydrogen (sodium amalgam); likewise its production from lactic and glyceric acids when these are heated with hydriodic acid:—

$$\underset{\text{Lactic Acid.}}{CH_3.CH(OH).CO_2H} + 2HI = CH_3.CH_2.CO_2H + H_2O + I_2.$$

Propionic acid is a colorless liquid, of penetrating odor, with specific gravity 0.992 at 18°, and boiling at 140°. Calcium chloride separates it from its aqueous solution, in the form of an oily liquid.

The *barium salt*, $(C_3H_5O_2)_2Ba + H_2O$, crystallizes in rhombic prisms. The *silver salt*, $C_3H_5O_2Ag$, consists of fine needles, soluble in 119 parts water at 17°. Its *ethyl ester* boils at 98°.

Substitution Products.—By the replacement of one hydrogen atom in propionic acid, two series of mono-derivatives, termed the α- and β-derivatives, arise:—

$$\underset{\alpha\text{-Derivative.}}{CH_3.CHX.CO_2H} \qquad \underset{\beta\text{-Derivative.}}{CH_2X.CH_2CO_2H.}$$

The isomeric compounds of the higher fatty acids are similarly designated as α-, β-, γ-, etc.

Whenever bromine is introduced into the fatty acids, it occupies preferably the α- position. In the formation of the halogen derivatives from the unsaturated acids by addition of the halogen hydride, the halogen enters in preference the β- or γ- position (see *Berichte*, **22**, Ref. 742):—

$$\underset{\text{Acrylic Acid.}}{CH_2:CH.CO_2H} + HI = \underset{\beta\text{-Iodpropionic Acid.}}{CH_2I.CH_2.CO_2H.}$$

The α-halogen acids yield α-oxy-acids when heated with aqueous bases, whereas the β-derivatives readily part with a halogen hydride, and become unsaturated acids (*Annalen*, 219, 322):—

$$CH_2Cl.CH_2.CO_2H \qquad \underset{\text{Acrylic Acid.}}{CH_2:CH.CO_2H} + HCl.$$

From the γ-acids originate salts of γ-oxy-acids through the action of bases. When in free condition they change to lactones. The alkaline carbonates immediately convert them into the latter.

α-**Chlorpropionic Acid**, $C_3H_5ClO_2$, is obtained by the decomposing action of water upon lactyl chloride (see lactic acid):—

$$CH_3.CHCl.COCl + H_2O = CH_3.CHCl.CO.OH + HCl.$$

It is a thick liquid, of specific gravity 1.28, and boils at 186°. When heated with moist oxide of silver, it becomes α-lactic acid. The *ethyl ester* boils at 146°. It is obtained by the action of alcohol upon lactyl chloride.

β-**Chlorpropionic Acid,** $C_3H_5ClO_2$, is produced by the action of chlorine water upon β-iodpropionic acid, and the addition of HCl to acrylic acid:—

$$CH_2{:}CH.CO_2H + HCl = CH_2Cl.CH_2.CO_2H.$$

Also upon heating β-oxypropionic acid (hydracrylic acid) to 120° with fuming hydrochloric acid.

It is crystalline, and melts at 41.5°. The *ethyl ester* boils at 155° (162°).

α-**Brompropionic Acid,** $C_3H_5BrO_2$, is produced by the direct bromination of propionic acid in the presence of bromine (*Berichte*, 22, 162), and when α-lactic acid is treated with HBr. It is crystalline, melts at 24.5°, and boils near 202°. The *ethyl ester* boils about 162°.

β-**Brompropionic Acid,** $C_3H_5BrO_2$, is formed when bromine water acts on β-iodpropionic acid, or by the addition of HBr to acrylic acid, and when hydracrylic acid is heated with hydrobromic acid. The acid crystallizes, and melts at 61.5°.

α-**Iodpropionic Acid,** $C_3H_5IO_2$, is produced by acting on α lactic acid, with phosphorus iodide. It is an oily liquid.

β-**Iodpropionic Acid,** $C_3H_5IO_2$, forms when PI_3 and water are allowed to act on glyceric acid (*Annalen*, 191, 284):—

$$CH_2.OH.CH(OH).CO_2H + 3HI = CH_2I.CH_2.CO_2H + I_2 + H_2O,$$

and when HCl is added to acrylic acid. To prepare it, treat crude glyceric acid with iodine and phosphorus (*Berichte*, 21, 24). The acid crystallizes in large, colorless, six-sided plates, with peculiar odor. They melt at 85°. Hot water dissolves the acid readily. Heated with concentrated hydriodic acid, it is reduced to propionic acid. The ethyl ester boils at 202° (*Berichte*, 21, 97).

β-**Nitropropionic Acid,** $CH_2(NO_2).CH_2.CO_2H$. This is formed, like the nitro-paraffins (p. 107), by the action of silver nitrite upon β-iodpropionic acid. It is very readily soluble in water, alcohol and ether. It crystallizes from chloroform in brilliant scales, melting at 66–67°. Reduced with tin and hydrochloric acid it becomes β-amidopropionic acid. The *ethyl ester*, obtained from β-iodpropionic ester, boils from 161–165°.

α-**Isonitroso-propionic Acid,** $CH_3.C(N.OH).CO_2H$, is a white, crystalline powder, made from acetyl carboxylic acid and methyl aceto-acetic ester (p. 214). It decomposes at 177° without fusing. Reduction converts it into α-amidopropionic acid (Alanine).

The *ethyl ester* consists of shining crystals, melting at 94°, and boiling at 233°. It is also formed when nitrous acid acts upon isosuccinic ester (*Berichte*, 20, 533).

The *disubstitution products* of propionic acid may exist in three isomeric forms:—

$CH_3.CX_2.CO_2H$	$CH_2.X.CHX.CO_2H$	$CHX_2.CH_2.CO_2H.$
α-Derivatives.	αβ Derivatives.	β-Derivatives.

The derivatives of the homologous acids are similarly named. The α-derivatives are almost the exclusive product in the chlorination and bromination of the fatty acids or their derivatives. The addition of chlorine or bromine (best in CS_2 solution) to the unsaturated acids converts them into αβ-derivatives:—

$$CH_2{:}CH.CO_2H + Br_2 = CH_2Br.CHBr.CO_2H.$$

Boiling water scarcely affects the α-derivatives; but the αβ-compounds become halogen hydroxy-acids:—

$$CH_2Cl.CH(OH).CO_2H \text{ and } CH_2(OH).CHCl.CO_2H.$$

The alkalies convert these into anhydride or ether-acids (glycide acids).

α-Dichlorpropionic Acid, $CH_3.CCl_2.CO_2H$, is obtained from dichlorpropionitrile, $CH_3.CCl_2.CN$ (by chlorination of propionitrile), with sulphuric acid (see p. 211). The ethyl ester may be formed from pyroracemic acid, $CH_3.CO.CO_2H$, by the action of PCl_5 and the decomposition of the chloride produced at first with alcohol. It is a liquid that boils at 185°–190°, solidifies below 0°, and is volatilized in a current of steam. The *ethyl ester*, $C_3H_3Cl_2.O_2.C_2H_5$, boils at 156°–157°; its *chloride* boils at 105°–115°, and the *amide*, $CH_3.CCl_2.CO.NH_2$, melts at 116°.

When the aqueous solution of the α-dichlorpropionates are boiled, they sustain decomposition. Zinc and sulphuric acid convert the acid into propionic acid. The silver salt changes to $CH_3.CO.CO_2H$ (pyroracemic acid), and α-dichlorpropionic acid (see *Berichte*, 18, 1227). α-Chloracrylic acid is produced on boiling with alcoholic potash. Zinc and hydrochloric acid convert it into propionic acid.

αβ-Dichlorpropionic Acid, $CH_2Cl.CHCl.CO_2H$, follows from the oxidation of dichlorhydrin, $CH_2Cl.CHCl.CH_2.OH$ (from glycerol and allyl alcohol, p. 134), also by heating α-chloracrylic acid (melting at 64°) to 100° with HCl (*Berichte*, 10, 1599), and by heating glyceric acid with hydrochloric acid (together with chlorlactic acid, *Berichte*, 12, 178). If PCl_5 be allowed to act upon glyceric acid, the chloride, $CH_2Cl.CHCl.COCl$, forms, and this yields the ester of the αβ-acid when treated with alcohol. αβ-Dichlorpropionic acid crystallizes in fine needles which melt at 50° and boil at 210°, suffering slight decomposition. The *ethyl ester* boils at 184°.

β-Dichlorpropionic Acid, $CHCl_2.CH_2.CO_2H$, is produced by heating β-chloracrylic acid with hydrochloric acid. It melts at 56°, and is reconverted by caustic potash into β-chloracrylic acid (*Berichte*, 20, Ref. 415).

α-Dibrompropionic Acid, $CH_3.CBr_2.CO_2H$, is obtained by heating propionic acid or α-brompropionic acid with bromine (*Berichte*, 18, 235). It crystallizes in quadratic tables, melting at 61°, and boils, with slight decomposition, at 220°. The *ethyl ester* is a liquid with camphor-like odor, and boils at 190°. The salts of the acid are tolerably stable. Zinc and sulphuric acid reduce it at once to propionic acid. Alcoholic potash changes it to α-bromacrylic acid, $CH_2{:}CBr.CO_2H$, and the latter combines with HBr and becomes αβ-dibrompropionic acid. When the α-dibrom-acid is heated to 100°, with fuming HBr, it is transformed into an isomeric αβ-dibrom-acid. It is very probable that α-bromacrylic acid forms at first and then takes on HBr.

αβ-Dibrompropionic Acid, $CH_2Br.CHBr.CO_2H$, is produced by oxidizing dibromhydrin, $CH_2Br.CHBr.CH_2OH$ (dibromallyl alcohol, p. 134), and acroleïn dibromide (p. 199) with nitric acid; also by adding Br_2 to acrylic acid and HBr to α-bromacrylic acid. This compound is capable of existing in two allotropic modifications, which can be readily converted one into the other. The one form melts at 51°, the other, more stable, at 64°. The acid boils at 227°, with partial decomposition. The *ethyl ester* has a fruit-like odor, and boils at 211°–214°.

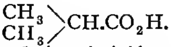
The salts are very stable. Zinc and sulphuric acid reduce the acid first to acrylic acid. Potassium iodide effects the same. Alcoholic potash changes the acid to α-bromacrylic acid. Brom-lactic acid is produced by digesting the silver salt with water (*Berichte*, 18, 236). The product is glyceric acid if an excess of silver oxide has been employed.

4. Butyric Acids, $C_4H_8O_2$.

Two isomeric acids are possible:—

$$CH_3.CH_2.CH_2.CO_2H$$

Normat Butyric Acid.



$$\begin{matrix}CH_3\\CH_3\end{matrix}\Big\rangle CH.CO_2H.$$

Isobutyric Acid.

(1) **Normal Butyric Acid**, butyric acid of fermentation, occurs free and also as the glycerol ester in the vegetable and animal kingdoms, especially in the butter of cows. It exists as hexyl ester in the oil of *Heracleum giganteum*, and as octyl ester in *Pastinaca sativa*. It is produced in the butyric fermentation of sugar, starch and lactic acid, in the decay or oxidation of normal butyl alcohol, and by the action of nascent hydrogen upon crotonic acid, $C_4H_6O_2$. It is prepared synthetically from propyl cyanide (butyronitrile) on boiling with alkalies or acids:—

$$C_3H_7.CN + 2H_2O = C_3H_7.CO_2H + NH_3;$$

also, from ethylic-aceto-ethyl acetate, and ethylmalonic acid (p. 212); hence the term ethyl acetic acid.

Ordinarily the acid is obtained by the fermentation of sugar or starch, induced by the previous addition of decaying substances. According to *Fitz*, the butyric fermentation of glycerol or starch is most advantageously evoked by the direct addition of schizomycetes, especially butyl-bacillus and Bacillus subtilis (*Berichte*, 11, 49, 53).

Butyric acid is a thick, rancid-smelling liquid, which solidifies when cooled. It boils at 163°; its specific gravity equals 0.9587 at 20°. It dissolves readily in water and alcohol, and may be thrown out of solution by salts. The *ethyl ester* boils at 120°.

The butyrates dissolve readily in water. The barium salt, $(C_4H_7O_2)_2Ba + 5H_2O$, crystallizes in pearly leaflets. The calcium salt, $(C_4H_7O_2)_2Ca + H_2O$ (*Annalen*, 213, 67), also yields brilliant leaflets, and is less soluble in hot than in cold water (in 3.5 parts at 15°); therefore the latter grows turbid on warming. Silver nitrate precipitates silver butyrate in shining needles from solutions of the butyrates. It is soluble in 400 parts water at 14°.

The butyrates unite to double salts with the acetates; these behave like salts of a butyro-acetic acid, $C_4H_8O_2.C_2H_4O_2$. The free acid appears in the fermentation of calcium tartrate; when distilled, it breaks up into butyric and acetic acids.

γ–**Chlorbutyric Acid**, $CH_2Cl.CH_2.CH_2.CO_2H$, has been prepared from γ-chlor-trimethylenecyanide. It solidifies in the cold and melts at 10°. When distilled it yields HCl and γ-caprolactone (see this).

αβ-**Dichlorbutyric Acid,** $CH_3.CHCl.CHCl.CO_2H$. This results upon the addition of chlorine to crotonic acid. It melts at 63°. With KOH it forms chlorisocrotonic acid (*Berichte*, 20, 1008).

Trichlorbutyric Acid, $C_4H_5Cl_3O_2$, appears in the oxidation of trichlorbutyraldehyde or alcohol (p. 197), in the cold, with concentrated nitric acid, or by means of chlorine. It consists of needles, melting at 60° and soluble in 25 parts of water. *β*-Chlorcrotonic acid is formed when the trichlor-acid is boiled with zinc and water: $C_4H_5Cl_3O_2 + Zn = C_4H_5ClO_2 + ZnCl_2$.

Bromine converts butyric acid into *α*-**Brombutyric Acid,** $CH_3CH_2.CHBr.CO.OH$, which boils about 215°. Alcoholic potash changes this to crotonic acid. Its *ethyl ester* boils at 178°. With CNK the latter yields *α*-cyanbutyric ester, boiling at 208°.

β-**Brombutyric Acid,** $CH_3.CHBr.CH_2.CO_2.H$, is produced (together with a little *α*-acid) on heating crotonic acid with hydrobromic acid. Crotonic acid combines with bromine to form *αβ*-dibrombutyric acid, $CH_3.CHBr.CHBr.CO_2H$, which melts near 87°.

γ-**Brom-** and **Iodobutyric** acids result from butyrolactone (see this) by the action of HBr and HI; the first melts at 33°, the second at 41° (*Berichte*, 19, Ref. 165).

β-**Iod-butyric Acid** is obtained by the union of crotonic acid and isocrotonic acid with hydriodic acid; it melts at 110° (*Berichte*, 22, Ref. 741).

α-**Isonitroso-butyric Acid,** $C_2H_5.C(N.OH).CO_2H$, obtained from ethylic aceto-ethyl acetate (p. 214), consists of silky needles, melting with decomposition at 152°. The *β*-**Isonitroso Acid,** $CH_3.C(N.OH).CH_2CO_2H$, from ethyl acetoacetic ester and hydroxylamine, melts with decomposition at 140°.

When a saturated solution of calcium butyrate is heated for some time it slowly passes into calcium isobutyrate (*Annalen*, **181**, 126).

(2) **Isobutyric Acid,** $(CH_3)_2.CH.CO_2H$, dimethyl-acetic acid, is found free in carobs (*Ceratonia siliqua*), as octyl ester in the oil of *Pastinaca sativa*, and as ethyl ester in croton oil. It is prepared by oxidizing isobutyl alcohol, and from isopropyl cyanide:—

$$C_3H_7.CN + 2H_2O = C_3H_7.CO_2H + NH_3.$$

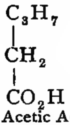
It is also obtained from dimethyl-aceto-acetic ester and from dimethyl malonic acid (p. 212), therefore the name dimethyl acetic acid.

Isobutyric acid bears great similarity to normal butyric acid, but is not miscible with water, and boils at 155°. Its specific gravity at 20° is 0.9490. It is soluble in 5 parts of water.

The *calcium salt*, $(C_4H_7O_2)_2Ca + 5H_2O$, crystallizes in monoclinic prisms and dissolves more readily in hot than in cold water. The silver salt, $C_4H_7O_2Ag$, consists of shining leaflets soluble in 110 parts H_2O at 16°. The *ethyl ester* boils at 110°; its specific gravity = 0.89 at 0°. Potassium permanganate oxidizes it to *α*-oxyisobutyric acid.

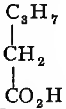
α-**Bromisobutyric Acid,** $(CH_3)_2.CBr.CO_2H$, is produced when isobutyric acid is heated with bromine to 140°. It crystallizes in white tables, melting at 48°, and boiling at 198°-200°. The *ethyl ester* boils at 163° (corr.); its sp. gr. = 1.328 at 0°. Moist silver oxide or barium hydrate converts it into *α* oxyisobutyric acid, $(CH_3)_2.C(OH).CO_2H$. When boiled together with silver it yields tetramethyl succinic acid and trimethyl glutaric acid.

5. **Valeric Acids,** $C_5H_{10}O_2$. There are four possible isomerides:—

1. 

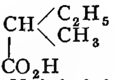
$$\begin{array}{c} C_3H_7 \\ | \\ CH_2 \\ | \\ CO_2H \end{array}$$

Propyl Acetic Acid.
Normal Valeric Acid.

2. 

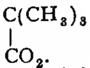
$$\begin{array}{c} C_3H_7 \\ | \\ CH_2 \\ | \\ CO_2H \end{array}$$

Isopropyl
Acetic Acid.
Isovaleric Acid.

3. 

$$\begin{array}{l} CH\langle^{C_2H_5}_{CH_3} \\ | \\ CO_2H \end{array}$$

Methyl-ethyl
Acetic Acid.

and 4. 

$$\begin{array}{l} C(CH_3)_3 \\ | \\ CO_2. \end{array}$$

Trimethyl
Acetic Acid.

(1) **Normal Valeric Acid,** $CH_3.(CH_2)_3.CO_2H$, formed in the oxidation of normal amyl alcohol and from butyl cyanides, is similar to butyric acid, but is more sparingly soluble in water (1 part in 27 parts at 16°). It boils at 186°. Its specific gravity at 0° equals 0.9568. It congeals in the cold, and melts at —20° (*Berichte*, 21, Ref. 649).

The α *isonitroso-acid*, $C_3H_7.C(N.OH).CO_2H$, derived from propyl aceto-acetic ester (p. 212), melts with decomposition at 144°. The γ *isonitroso-acid*, $CH_3.C(N.OH).CH_2.CH_2.CO_2H$, formed from lævulinic acid and hydroxylamine, fuses with decomposition at 96°, and when digested with sulphuric acid, passes into imido-lactone (*Berichte*, 20, 2671).

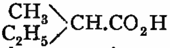
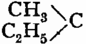
(2) **Isovaleric Acid,** $(CH_3)_2.CH.CH_2.CO_2H$, isopropyl acetic acid, or isobutyl carboxylic acid, is obtained from isobutyl cyanide, $C_4H_9.CN$, by saponification with alkalies, likewise from isopropyl aceto-acetic ester, and from isopropyl-malonic ester (see p. 212). It is an oily liquid with an odor resembling that of old cheese; possesses a specific gravity of 0.947, and boils at 174°. It is optically inactive.

The isovalerates generally have a greasy touch. When thrown in small pieces upon water they have a rotary motion, dissolving at the same time. The *barium* salt, $(C_5H_9O_2)_2Ba$, usually crystallizes in thin leaflets, and is soluble in 2 parts water at 18°. The *calcium* salt, $(C_5H_9O_2)_2Ca + 3H_2O$, forms rather stable, readily soluble needles. The officinal *zinc* salt, $(C_5H_9O_2)_2Zn + 2H_2O$, crystallizes in large, brilliant leaflets; when the solution is boiled a basic salt separates. The *silver* salt, $C_5H_9O_2Ag$, is very sparingly soluble in water (in 520 parts at 21°). The *ethyl ester*, $C_5H_9(C_2H_5)O_2$, boils at 135°.

α-Brom-isovaleric acid, $C_3H_7.CBr.CO_2H$, is formed in the bromination of isovaleric acid in the presence of phosphorus. It melts at 40° (*Berichte*, 21, Ref. 5). Silver converts its ester into two dipropylsuccinic acids (*Berichte*, 22, 48).

Potassium permanganate oxidizes isovaleric acid to β-oxyisovaleric acid, $(CH_3)_2.C(OH).CH_2.CO_2H$. Nitric acid attacks in addition the CH-group, forming methyloxysuccinic acid and β *nitroisovaleric acid*, $(CH_3)_2.C(NO_2).CH_2.CO_2H$, which crystallizes in large leaflets and is sparingly soluble in water; β-dinitropropane, $(CH_3)_2C(NO_2)_2$ (*Berichte*, 15, 2324), is produced at the same time.

Ordinary valeric acid occurs free, and as esters in the animal and vegetable kingdom, chiefly in the small valerian root (*Valeriana officinalis*), and in the root of *Angelica Archangelica*, from which it may be isolated by boiling with water or a soda solution. It is a mixture of isovaleric acid with the optically active methyl-ethyl acetic acid, and is therefore also active. A similar artificial mixture may be obtained by oxidizing the amyl alcohol of fermentation (p. 130) with a chromic acid solution. Inasmuch as the salts of methyl-ethyl acetic acid dissolve with difficulty, it is a general thing to obtain only isovalerates from the ordinary valeric acid. Valeric acid combines with water and yields an officinal hydrate, $C_5H_{10}O_2 + H_2O$, soluble in 26.5 parts of water at 15°.

(3) **Methyl-ethyl Acetic Acid,** $\begin{matrix}CH_3\\C_2H_5\end{matrix}\!>\!CH.CO_2H$ (active valeric acid), is obtained by synthesis from methyl-ethyl-aceto-acetic ester, from methyl-ethyl-malonic ester (p. 212), and from the so-called methyl-ethyl oxalic acid, $\begin{matrix}CH_3\\C_2H_5\end{matrix}\!>\!C(OH).CO_2H$ (see this); also from methylcrotonic acid (p. 241), $C_5H_8O_2$, by addition of 2H (when heated with HI), and from brom- and iodmethyl ethyl acetic acid (from methylcrotonic acid and angelic acid) by reduction with sodium amalgam.

The acid possesses a valerian-like odor, boils at 175° and has a specific gravity of 0.941 at 21°. The *calcium* salt, $(C_5H_9O_2)_2Ca + 5H_2O$, crystallizes in brilliant needles which slowly effloresce in the air. The *barium* salt, $(C_5H_9O_2)_2Ba$, is a *gummy amorphous* mass, and is not crystallizable. The *silver* salt, $C_5H_9O_2Ag$, is much more soluble than that of the isovaleric acid (in 88 parts at 20°) and crystallizes in groups of feather-shaped, shining needles.

The synthesized methyl-ethyl acetic acid is optically inactive. *An active modification* is present in the naturally occurring valeric acid, and is obtained by the oxidation of the amyl alcohol of fermentation (see above). The silver salt affords a means of separating it from the accompanying isovaleric acid (*Annalen*, 204, 159). The active acid has not yet been isolated in a pure condition; otherwise it exhibits all the properties of the inactive variety, and yields perfectly similar salts.

(4) **Trimethyl Acetic Acid,** $(CH_3)_3C.CO_2H$ (Pinalic acid), is formed from tertiary butyl iodide, $(CH_3)_3CI$ (p. 131), by means of the cyanide, also by the oxidation of pinacoline (p. 210). It is a leafy, crystalline mass, melting at 35° and boiling at 163°. The acid is soluble in 40 parts H_2O at 20°, and has an odor resembling that of acetic acid.

The *barium* salt, $(C_5H_9O_2)_2Ba + 5H_2O$, and *calcium* salt, $(C_5H_9O_2)_2Ca + 5H_2O$, crystallize in needles or prisms. The *silver* salt, $C_5H_9O_2Ag$, is precipitated in glistening, flat needles. The *ethyl ester*, $C_5H_9O_2.C_2H_5$, boils at 118.5°.

The Hexoic or Caproic Acids, $C_6H_{12}O_2 = C_5H_{11}.CO_2H$.

Eight isomerides are theoretically possible (because there are eight C_5H_{11} (amyl) groups). Seven of these have been prepared. We may mention:—

(1) **Normal Caproic Acid or Hexoic Acid,** $CH_3(CH_2)_4.CO_2H$, which is produced in the fermentation of butyric acid, and may be obtained by the oxidation of normal hexyl alcohol, and from normal amyl cyanide, $C_5H_{11}.CN$. In addition, it forms when butyl iodide acts on aceto-acetic ester. It is an oily liquid that has a sp. gr. of 0.928 at 20°, boils at 205°, solidifies in the cold and melts at —2°. Its *barium* salt, $(C_8H_{11}O_2)_2Ba + 3H_2O$, is soluble in 9 parts of water at 10°. The *ethyl ester* boils at 167°.

(2) **Isobutyl Acetic Acid,** $(CH_3)_2.CH.CH_2.CO_2H$, is obtained from isoamyl cyanide and from isobutyl aceto-acetic ester (p. 212). Some fats apparently contain it. It has a specific gravity of 0.931 at 15° and boils at 200°. The *ethyl ester* boils at 161°. By the oxidation of isobutyl acetic acid with potassium permanganate the lactone of γ-oxy-isocaproic acid, $(CH_3)_2.C(OH).CH_2.CH_2.CO_2H$, is formed.

(3) **Methylpropyl Acetic Acid,** $\begin{matrix}C_3H_7\\CH_3\end{matrix}\rangle CH.CO_2H$, is prepared from methylpropyl carbinol (p. 131) through the cyanide and from α-methyl valerolactone (from saccharin) by reduction with HI. It boils at 198° and has the specific gravity 0.941 at 0° (*Berichte*, 16, 1832). The same acid has been obtained from isosaccharin (*Berichte*, 18, 633).

Heptoic Acids, $C_7H_{14}O_2 = C_6H_{13}.CO_2H$.

Six of the seventeen possible isomerides are known.

(1) **Normal Heptoic or Œnanthylic Acid,** $CH_3(C_2H_5)_5.CO_2H$, is produced by the oxidation of œnanthol (p. 198) with nitric acid, and also from normal hexyl cyanide, $C_6H_{13}.CN$. It is a fatty-smelling oil, boiling near 223°, and solidifying, when cooled, to a crystalline mass, which melts at —10.5°. The *ethyl ester* boils at 188°.

(2) **Methyl-n-butyl Acetic Acid,** $\begin{matrix}CH_3\\C_4H_9\end{matrix}\rangle CH.CO_2H$, obtained synthetically from aceto-acetic ester, has been prepared by reducing lævulo-carboxylic acid. It boils at 210° (*Berichte*, 19, 224).

(3) **Ethyl-n-propyl Acetic Acid,** $\begin{matrix}C_2H_5\\C_3H_7\end{matrix}\rangle CH.CO_2H$, from aceto-acetic ester, boils at 209° (*Berichte* 19, 227).

The Octoic Acids, $C_8H_{16}O_2 = C_7H_{15}.CO_2H$.

Normal Octoic or Caprylic Acid is present in fusel oil, and as glycerol ester in many oils and fats. It is produced by the oxidation of fats and oleic acid with nitric acid; also obtained from normal octyl alcohol. The acid crystallizes in needles or leaflets, which melt at 16°–17°, and boil at 236°–237°. The barium salt is soluble in 50 parts boiling water, and crystallizes in fatty tablets.

Nonoic Acid, $C_9H_{18}O_2$, **Pelargonic Acid,** occurs in the leaves of *Pelargonium roseum*, and is prepared by the oxidation of oleic acid and oil of rue (methyl nonyl ketone, p. 210), with nitric acid. It may also be obtained from normal octyl cyanide, $C_8H_{17}.CN$, and by the fusion of undecylenic acid (p. 242) with potassium hydroxide. It is, therefore, the normal nonoic acid. It fuses at + 12.5° and boils at 253°–254°.

HIGHER FATTY ACIDS.

These (p. 215) are chiefly solids at ordinary temperatures, and can usually be distilled without suffering decomposition. They are volatilized by superheated steam. They are insoluble in water, but readily soluble in alcohol and ether, from which they may be crystallized out. In the naturally occurring oils and solid fats, they exist in the form of glycerol esters (see these). When fats are saponified by potassium or sodium hydroxide, salts of the fatty acids—*soaps*—are produced. The sodium salts are solids and hard, while those with potassium are soft. Salt water will convert potash soaps into sodium soaps. In small quantities of water the salts of the alkalies dissolve completely, but with an excess of water they suffer decomposition, some alkali and fatty acid being liberated. The action of soap depends on this fact. The remaining metallic salts of the fatty acids are sparingly soluble or insoluble in water, but generally dissolve in alcohol. The lead salts, formed directly by boiling fats with litharge and water, constitute the so-called *lead plaster*.

The natural fats almost invariably contain several fatty acids (frequently, too, oleic acid). To separate them, the acids are set free from their alkali salts by means of hydrochloric acid and then fractionally crystallized from alcohol. The higher, less soluble acids separate out first. The separation is more complete if the acids be fractionally precipitated (see p. 216). The free acids are dissolved in alcohol, saturated with ammonium hydroxide and an alcoholic solution of magnesium acetate added. The magnesium salt of the higher acid will separate out first, this is then filtered off and the solution again precipitated with magnesium acetate. The acids obtained from the several fractions are subjected anew to the same treatment, until, by further fractionation, the melting point of the acid remains constant—an indication of purity. The melting point of a mixture of two fatty acids is usually lower than the melting points of both acids (the same is the case with alloys of the metals).

The fatty acids existing in fats and oils all possess the normal structure of the carbon chains, inasmuch as they yield only lower and normal acids when oxidized. It is an interesting fact, that in the natural fats only acids exist that have an even number of carbon atoms. Those that possess an uneven number of carbon atoms (as undecylic and tridecylic) are artificially prepared by the oxidation of their corresponding ketones (p. 200). The latter are obtained by distilling the calcium salt of an acid having one carbon atom more, with calcium acetate. In this manner there is derived from lauric acid, $C_{11}H_{23}.CO_2H$, the ketone, $C_{11}H_{23}.CO.CH_3$, which is oxidized to undecylic acid, $C_{11}H_{22}O_2 = C_{10}H_{21}.CO_2H$, by chromic acid. Undecylic acid yields the ketone, $C_{10}H_{21}.CO.CH_3$, and this the acid, $C_{10}H_{20}O_2$, etc. Thus, starting with the highest acid, we can successively form all the lower members of the series.

Capric Acid, $C_{10}H_{20}O_2$, present in butter, in cocoanut oil and in many fats, forms a crystalline mass, melting at 31.4°, and boiling, with partial decomposition, at 268°–270°. The *barium* salt crystallizes from alcohol in fatty, shining needles or scales. The *ethyl ester* is a liquid, and possesses a fruit-like odor. It boils at 243°.

Undecylic Acid, $C_{11}H_{22}O_2$, is obtained by oxidation from undecyl-methyl ketone, $C_{11}H_{23}.CO.CH_3$ (see above), and from undecylenic acid, when the latter is heated with hydriodic acid. It is a scaly, crystalline mass, which melts at 28.5°, and boils at 212° under a pressure of 100 mm. An acid obtained from the fruit of the California bay-tree appears to be identical with the preceding acid.

Lauric Acid, $C_{12}H_{24}O_2$, occurs as glycerol-ester in the fruit of *Laurus nobilis* and in pichurium beans. It crystallizes in large, brilliant needles, melting at 43.6°. The *ethyl ester* possesses a fruit-like odor, and boils at 269°.

Tridecylic Acid, $C_{13}H_{26}O_2$, is formed by the oxidation of tridecyl-methyl ketone, $C_{13}H_{27}CO.CH_3$ (from myristic acid), and crystallizes in scales, which melt at 40.5° and under 100 mm. pressure boil at 235°.

Myristic Acid, $C_{14}H_{28}O_2$, obtained from muscat butter (from *Myristica moschata*), from spermaceti and oil of cocoanut, is a shining, crystalline mass, melting at 54°. The *ethyl ester* is solid.

Pentadecatoic Acid, $C_{15}H_{30}O_2$, is prepared from pentadecato-methyl ketone, $C_{15}H_{31}.CO.CH_3$ (from palmitic acid); it melts at 51°, and boils under a pressure of 100 mm. at 257°.

Palmitic Acid, $C_{16}H_{32}O_2$. The glycerol-ester of this acid and that of stearic acid constitute the principal ingredients of solid animal fats. The stearin employed in the candle manufacture is a mixture of free palmitic and stearic acids. Palmitic acid occurs in rather large quantities, partly uncombined, in palm oil. Spermaceti is the cetyl-ester of the acid, while the myricyl ester is the chief constituent of beeswax. The acid is most advantageously obtained from olive oil, which consists almost exclusively of the glycerides of palmitic and oleic acid (see latter); also, from Japanese beeswax, a glyceride of palmitic acid (*Berichte*, 21, 2265). The acid is artificially made by heating cetyl alcohol with soda-lime:—

$$C_{16}H_{31}.CH_2.OH + KOH = C_{16}H_{31}.CO_2K + 2H_2;$$

also by fusing together oleic acid and potassium hydroxide.

Palmitic acid crystallizes in white needles, which melt at 62°, and solidify to a crystalline mass.

Margaric Acid, $C_{17}H_{34}O_2$, does not apparently exist naturally in the fats. It is made in an artificial way by boiling cetyl cyanide with caustic potash:—

$$C_{16}H_{33}.CN + 2H_2O = C_{16}H_{33}.CO_2H + NH_3.$$

The acid bears great resemblance to palmitic acid, and melts at 59.9°.

Stearic Acid, $C_{18}H_{36}O_2$, is associated with palmitic and oleic acids as a mixed ether in solid animal fats, the tallows. The acid crystallizes from alcohol in brilliant leaflets, melting at 62.2°.

The so-called *stearin* of candles consists of a mixture of stearic and palmitic acids. For its preparation, beef tallow and suet, both solid fats, are saponified with potassium hydroxide or sulphuric acid. The acids which separate are distilled with superheated steam. The yellow, semi-solid distillate, a mixture of stearic, palmitic and oleic acids, is freed from the liquid oleic acid by pressing it between warm plates. The residual, solid mass is then fused together with some wax or paraffin, to prevent crystallization occurring when the mass is cold, and molded into candles.

Cetyl Acetic Acid, $C_{16}H_{33}.CH_2.CO_2H$, is probably identical with the above, and is obtained from cetyl aceto-acetic ester and cetyl malonic acid (see p. 212) (*Berichte*, 17, 1629). An isomeric acid, called *dioctyl acetic* acid $(C_8H_{17})_2CH.CO_2H$, is prepared from dioctyl-aceto-acetic ester and from dioctylmalonic acid. It melts at 38.5°.

We may briefly mention the following higher acids (see p. 215):—

Arachidic Acid, $C_{20}H_{40}O_2$, occurs in earth-nut oil (from *Arachis hypogæa*), and is composed of shining leaflets, melting at 75°. It has been obtained synthetically from aceto-acetic ester and octodecyl iodide (from stearyl aldehyde) (*Berichte*, 17, Ref. 570).

Cerotic Acid, $C_{27}H_{54}O_2$, or $C_{26}H_{52}O_2$ (see *Annalen*, 224, 225), occurs in a free condition in beeswax, and may be extracted from this on boiling with alcohol. As ceryl ester, it constitutes the chief ingredient of *Chinese wax*. On boiling the latter with an alcoholic potash solution, potassium cerotate and ceryl alcohol are produced. The acid may also be obtained by oxidizing ceryl alcohol, or by fusing it with KOH:—

$$C_{27}H_{56}O + KOH = C_{27}H_{53}O_2K + 2H_2.$$

It crystallizes from alcohol in delicate needles, melting at 78°.

Melissic Acid, $C_{30}H_{60}O_2$, is formed from myricyl alcohol (p. 134) when the latter is heated with soda-lime. It is a waxy substance, melting at 88°, and is really, as it appears, a mixture of two acids. The so-called **Theobromic Acid**, $C_{64}H_{128}O_2$, obtained from cacao butter, melts at 72°, and is apparently identical with arachidic acid.

2. UNSATURATED ACIDS, $C_nH_{2n-2}O_2$.

Acrylic Acid, $C_3H_4O_2 = C_2H_3.CO_2H$
Crotonic " $C_4H_6O_2 = C_3H_5.CO_2H$
Angelic " $C_5H_8O_2 = C_4H_7.CO_2H$
Pyroterebic " $C_6H_{10}O_2 = C_5H_9.CO_2H$

Oleic Acid, $C_{18}H_{34}O_2$ — Erucic Acid, $C_{22}H_{42}O_2$.

The acids of this series, bearing the name *Oleic Acids*, differ from the fatty acids by containing two atoms of hydrogen less than the latter. They also bear the same relation to them that the alcohols of the allyl series do to the normal alcohols. We can consider them derivatives of the alkylens, C_nH_{2n}, produced by the replacement of one atom of hydrogen by the carboxyl group. In this manner their possible isomerides are readily deduced.

As unsaturated compounds the oleic acids are capable of combining directly with two affinities, when the double union of the two carbon atoms becomes simple. Hence they unite directly with the halogens and halogen hydrides:—

$$\underset{\text{Acrylic Acid.}}{CH_2:CH.CO_2H} + Br_2 = \underset{\alpha\beta\text{-Dibrompropionic Acid.}}{CH_2Br.CHBr.CO_2H.}$$

On combining with two hydrogen atoms they become fatty acids:—

$$\underset{\text{Acrylic Acid.}}{CH_2{:}CH.CO_2H} + H_2 = \underset{\text{Propionic Acid.}}{CH_3.CH_2.CO_2H}.$$

The lower members, as a general thing, combine readily with the H_2 evolved in the action of zinc upon dilute sulphuric acid; while the higher remain unaffected. All may be hydrogenized, however, by heating with hydriodic acid and phosphorus (*Berichte*, 12, Ref. 376). The union with halogen hydrides occurs somewhat differently than observed with the alkylens. The halogen atom does not, as in the latter instance, attach itself to the carbon atom carrying the least number of hydrogen atoms, but prefers the β or γ position (p. 225).

The methods employed for the preparation of the unsaturated acids are similar to those used with the fatty acids, since the latter can be obtained from the unsaturated compounds by analogous methods. They are formed from the saturated fatty acids by the withdrawal of two hydrogen atoms, just as the alkylens are derived from the normal hydrocarbons:—

(1) Like the fatty acids they are produced by the oxidation of their corresponding alcohols and aldehydes; thus allyl alcohol and its aldehyde afford acrylic acid:—

$$\underset{\text{Allyl Alcohol.}}{CH_2{:}CH.CH_2.OH} \text{ and } \underset{\text{Acroleïn.}}{CH_2{:}CH.CHO} \text{ yield } \underset{\text{Acrylic Acid.}}{CH_2{:}CH.CO_2H}.$$

(2) Some may be prepared synthetically from the halogen derivatives, $C_nH_{2n-1}X$, aided by the cyanides (see p. 211); thus allyl iodide yields allyl cyanide and crotonic acid:—

$$C_3H_5I \text{ forms } C_3H_5.CN \text{ and } C_3H_5.CO_2H.$$

The replacement of the halogen by CN in the compounds $C_nH_{2n-1}X$ is conditioned by the structure of the latter. Although allyl iodide, $CH_2{:}CH.CH_2I$, yields a cyanide, ethylene chloride, $CH_2{:}CHCl$, and β-chlorpropylene, $CH_3.CCl{:}CH_2$, are not capable of this reaction.

(3) Another synthetic method is to introduce the allyl group, C_3H_5 (by means of allyl iodide), into aceto-acetic ester and malonic ester, and then further transpose the products first formed (p. 212). Allyl acetic acid, $C_3H_5.CH_2.CO_2H$, and diallyl acetic acid, $(C_3H_5)_2CH.CO_2H$, have been obtained in this manner.

(4) Some acids have been synthetically prepared by Perkins' reaction. This is readily executed with benzene derivatives. It consists in letting the aldehydes act upon a mixture of acetic anhydride and sodium acetate (compare Cinnamic Acid): $\underset{\text{Œnanthol.}}{C_6H_{13}CHO} + CH_3.CO_2Na = \underset{\text{Nonylenic Acid.}}{C_6H_{13}.CH = CH.CO_2Na} + H_2O$ (*Annalen*, 227, 79).

Pyroracemic acid acts analogously with sodium acetate; carbon dioxide splits off and crotonic acid results (*Berichte*, 18, 987).

(5) Unsaturated $\beta\gamma$-acids are prepared by distilling alkylized paraconic acids. Thus methyl-paraconic acid yields ethylidene propionic acid (*Berichte*, 23, Ref. 91): $C_6H_8O_4 = C_5H_8O_2 + CO_2$.

Generally, the unsaturated acids are prepared from the saturated by

(1) The action of alcoholic potash (p. 80) upon the monohalogen derivatives of the fatty acids :—

$$\underset{\alpha\text{-Chlorbutyric Acid.}}{CH_3.CH_2.CHCl.CO_2H} \text{ and } \underset{\beta\text{-Chlorbutyric Acid.}}{CH_3.CHCl.CH_2.CO_2H} \text{ yield } \underset{\text{Crotonic Acid.}}{CH_3.CH{:}CH.CO_2H}.$$

The β-derivatives are especially reactive, sometimes parting with halogen hydrides on boiling with water (p. 223). (The γ-halogen acids yield oxy-acids and lactones.) Similarly, the $\alpha\beta$-derivatives of the acids (p. 225) readily lose two halogen atoms, either by the action of nascent hydrogen—

$$\underset{\alpha\beta\text{-Dibrompropionic Acid.}}{CH_2Br.CHBr.CO_2H} + 2H = \underset{\text{Acrylic Acid.}}{CH_2{:}CH.CO_2H} + 2HBr,$$

or even more readily when heated with a solution of potassium iodide, in which instance the primary di-iod-compounds part with iodine (p. 99).

$$CH_2I.CHI.CO_2H = CH_2{:}CH.CO_2H + I_2.$$

(2) The removal of water (in the same manner in which the alkylens C_nH_{2n} are formed from the alcohols) from the oxy-fatty acids (the acids belonging to the lactic series) :—

$$\underset{\alpha\text{-Oxypropionic Acid.}}{CH_3.CH(OH).CO_2H} \text{ and } \underset{\beta\text{-Oxypropionic Acid.}}{CH_2(OH).CH_2.CO_2H} \text{ yield } \underset{\text{Acrylic Acid.}}{CH_2{:}CH.CO_2H}.$$

Here again the β-derivatives are most inclined to alteration, losing water when heated. The removal of water from α-derivatives is best accomplished by acting on the esters with PCl_5. The esters of the unsaturated acids are formed first, and can be saponified by means of alkalies.

(3) From the unsaturated dicarboxylic acids, containing two carboxyl groups attached to one carbon atom (see p. 212) :—

$$\underset{\text{Ethidene Malonic Acid.}}{CH_3.CH{:}C(CO_2H)_2} = \underset{\text{Crotonic Acid.}}{CH_3.CH{:}CH.CO_2H} + CO_2.$$

Like the saturated acids in their entire character, the unsaturated derivatives are, however, distinguished by their ability to take up additional atoms (p. 234). Their behavior, when fused with potassium or sodium hydroxide, is interesting, because it affords a means of ascertaining their structure. By this treatment their double union is severed and two monobasic fatty acids result :—

$$\underset{\text{Acrylic Acid.}}{CH_2{:}CH.CO_2H} + 2H_2O = \underset{\text{Formic Acid.}}{CH_2O_2} + \underset{\text{Acetic Acid.}}{CH_3.CO_2H} + H_2,$$

$$\underset{\text{Crotonic Acid.}}{CH_3CH{:}CH.CO_2H} + 2H_2O = \underset{\text{Acetic Acid.}}{CH_3.CO_2H} + \underset{\text{Acetic Acid.}}{CH_3.CO_2H} + H_2.$$

Oxidizing agents (chromic acid, nitric acid, permanganate of potash) have the same effect. The group linked to carboxyl is usually further oxidized, and thus a dibasic acid results.

When carefully oxidized with permanganate (see p. 82), the unsaturated acids sustain an alteration similar to that of the olefines; dioxy-acids result (Saytzeff, Fittig, Hazura, *Berichte*, 21, 919, 1648, 1878). For example, phenylacrylic acid yields phenylglyceric acid:—

$$\underset{\text{Phenylacrylic Acid.}}{C_6H_5.CH{:}CH.CO_2H} + O + H_2O = \underset{\text{Phenylglyceric Acid.}}{C_6H_5.CH(OH).CH(OH).CO_2H.}$$

When the unsaturated acids are heated to 100°, with KOH or NaOH, they frequently absorb the elements of water and pass into oxy-acids. Thus, from acrylic acid we obtain α-lactic acid ($CH_2{:}CH.CO_2H + H_2O = CH_3.CH(OH).CO_2H$), and malic from fumaric acid, etc.

---

1. **Acrylic Acid**, $C_3H_4O_2 = CH_2{:}CH.CO_2H$, the lowest member of this series, is obtained according to the general methods:—

(1) From iod-propionic acid by the action of alcoholic potash or lead oxide.

(2) From $\alpha\beta$-dibrompropionic acid by the action of zinc and sulphuric acid, or potassium iodide.

(3) By heating β-oxypropionic acid (hydracrylic acid).

The best method consists in oxidizing acroleïn with silver oxide.

The aqueous solution (3 parts H_2O) of acroleïn is mixed with silver oxide, digested for some time in the cold and then heated to boiling. Sodium carbonate is next added, the filtrate concentrated and distilled with dilute sulphuric acid. The acrylic acid in the distillate is converted into the silver or lead salt, which is decomposed by heating in a current of H_2S, that the acid may be obtained in an anhydrous condition.

Acrylic acid is a liquid with an odor like that of acetic acid, and solidifies at low temperatures to crystals melting at + 7°. It boils at 139–140°, and is miscible with water. If allowed to stand for some time it is transformed into a solid polymeride. By protracted heating on the water bath with zinc and sulphuric acid it is converted into propionic acid. This change does not occur in the cold. It combines with bromine to form $\alpha\beta$-dibrompropionic acid, and with the halogen hydrides to yield β-substitution products of propionic acid (p. 224). If fused with caustic alkalies it is broken up into acetic and formic acids.

The salts of acrylic acid, the silver salt excepted, are very soluble in water and crystallized with difficulty. They suffer decomposition when heated to 100°. The *silver salt*, $C_3H_3O_2Ag$, consists of shining needles which blacken at 100°. The *lead salt*, $(C_3H_3O_2)_2Pb$, crystallizes in long, silky, glistening needles.

The *ethyl ester*, $C_3H_3O_2.C_2H_5$, obtained from the ester of αβ-dibrompropionic acid by means of zinc and sulphuric acid, is a pungent-smelling liquid boiling at 101–102°. The *methyl ester* boils at 85°, and after some time polymerizes to a solid mass.

Substitution Products. There are two isomeric forms of mono-substituted acrylic acids (p. 223):—

$$\underset{\alpha\text{-Derivatives.}}{CH_2{:}CCl.CO_2H} \quad \text{and} \quad \underset{\beta\text{-Derivatives.}}{CHCl{:}CH.CO_2H.}$$

α-**Chloracrylic Acid** is probably the acid which results when αβ-dichlorpropionic acid is heated with alcoholic potash (*Berichte*, 18, 241). It crystallizes in needles, melts from 64–65°, and is even volatile at ordinary temperatures. It combines with HCl at 100° to produce αβ-dichlorpropionic acid (*Berichte*, 10, 1499; 18, 244).

β-**Chloracrylic Acid** is produced together with dichloracrylic acid in the reduction of chloralid with zinc and hydrochloric acid (*Annalen*, 239, 263), also from propiolic acid, $C_3H_2O_2$ (p. 244), by the addition of HCl. It crystallizes in leaflets and melts at 84° (*Annalen*, 203, 83). The *ethyl ester* boils at 142–144°, and is most easily obtained from the ester of trichlorlactic acid by reduction with zinc and hydrochloric acid in alcoholic solution. The *ester* of dichloracrylic acid is obtained at the same time.

α-**Bromacrylic Acid** is prepared from α- and αβ-dibrompropionic acids with alcoholic potash (*Berichte*, 14, 1867). It crystallizes in large plates melting at 69–70°. It combines with HBr to form αβ-dibrompropionic acid.

β-**Bromacrylic Acid** is obtained from the chloralid of tribromlactic acid when this is reduced with zinc and hydrochloric acid. It may also be prepared from propiolic acid by the addition of HBr (*Berichte*, 19, 541). It consists of fine needles, melting at 115–116°.

Iodoacrylic Acid, $C_3H_3IO_2$ (probably β), is obtained from propiolic acid by the addition of HI. It forms leaflets melting at 140°. There is also formed at the same time an acid melting at 65°, which probably is the second possible geometrical isomeride (*Berichte*, 19, 542).

There are two disubstituted acrylic acids:—

$$\underset{\alpha\beta\text{-Derivative.}}{CHX{:}CX.CO_2H} \quad \text{and} \quad \underset{\beta\text{-Derivative.}}{CX_2{:}CH.CO_2H.}$$

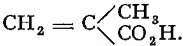
αβ-**Dibromacrylic Acid** is obtained from mucobromic acid and tribromsuccinic acid; and the β-**Dibromacrylic Acid** from the latter and also from brompropiolic acid by the addition of HBr (p. 245). Both acids melt from 85–86° (*Berichte*, 19, 1396).

αβ-**Di-iodo-acrylic Acid**, formed by the addition of iodine to propiolic acid, melts at 106°. β-**Di-iodo-acrylic Acid** is produced by the addition of HI to iodopropiolic acid. It melts at 133° (*Berichte*, 18, 2284).

2. THE CROTONIC ACIDS, $C_4H_6O_2 = C_3H_5.CO_2H$.

According to the current representations of the constitution of the unsaturated monocarboxylic acids three isomerides of the above formula are possible :—*

1. $CH_3 - CH = CH - CO_2H$ Normal Crotonic Acid. 2. $CH_2 = CH - CH_2 - CO_2H$ Isocrotonic Acid.

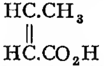
3.


$$CH_2 = C\begin{matrix}\diagup CH_3 \\ \diagdown CO_2H.\end{matrix}$$

Methylacrylic Acid.

The first formula is attributed to the ordinary solid crotonic acid, while the second is ascribed to the liquid isocrotonic acid. Yet it would seem that the same structural formula (1) belonged to both acids, and that relations existed here similar to those noted with maleïc and fumaric acids, for which the present structural formulas give no explanation.

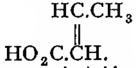
Following J. Wislicenus, it is assumed that crotonic and isocrotonic acids have the same structural formula. They are geometrical or stereochemical isomerides, corresponding to the formulas :—



$$\begin{matrix}HC.CH_3 \\ \| \\ HC.CO_2H\end{matrix}$$

Crotonic Acid.

and



$$\begin{matrix}HC.CH_3 \\ \| \\ HO_2C.CH.\end{matrix}$$

Isocrotonic Acid.

The first occupies the plane-symmetric and the second the central symmetric position (p. 52). This seems to be confirmed by the formation of ordinary crotonic acid from tetrolic acid by means of sodium amalgam (*Berichte*, **22**, 1183). The analogy with the two cinnamic acids, $C_6H_5.CH:CH.CO_2H$, favors this assumption. The differences between these last two acids cannot be explained by structural formulas.

Two mono-chloracids can be derived from each of the two stereo-isomeric crotonic acids (*Berichte*, **20**, Ref. 449; **22**, Ref. 51 and 816).

1. **Ordinary Crotonic Acid** is obtained :—

(1) By the oxidation of crotonaldehyde, $CH_3.CH:CH.COH$ (p. 199).

(2) By the dry distillation of β-oxybutyric acid, $CH_3.CH(OH).CH_2.CO_2H$.

(3) By the action of alcoholic potash upon α-brombutyric acid, and KI upon $\alpha\beta$-dibrombutyric acid.

(4) From allyl iodide by means of the cyanide.

(5) By the action of sodium amalgam on tetrolic acid (*Berichte*, **21**, Ref. 494).

---

* A supposed fourth crotonic acid, the so-called vinyl acetic acid (from the so-called vinylmalonic acid) appears identical with trimethyl carboxylic acid derived from trimethylene.

The most practicable method of obtaining crotonic acid is to heat malonic acid, $CH_2(CO_2H)_2$, with paraldehyde and acetic anhydride. The ethidene malonic acid first produced decomposes into CO_2 and crotonic acid (p. 235) (*Annalen*, 218, 147).

Crotonic acid crystallizes in fine, woolly needles or in large plates, which fuse at 72° and boil at 182°. It dissolves in 12 parts water at 20°. The warm aqueous solution will reduce alkaline silver solutions with the formation of a silver mirror. Zinc and sulphuric acid, but not sodium amalgam, convert it into normal butyric acid. It combines with HBr and HI to yield β-brom- and iodbutyric acid, and with chlorine and bromine to αβ-dichlor- and dibrombutyric acid. When fused with caustic potash, it breaks up into two molecules of acetic acid; nitric acid oxidizes it to acetic and oxalic acids.

α-**Chlorcrotonic Acid**, $CH_3.CH:CCl.CO_2H$, is obtained when trichlorbutyric acid (p. 227) is treated with zinc and hydrochloric acid, or zinc dust and water. Further, by the action of alcoholic potash on αβ-dichlorbutyric ester (*Berichte*, 21, Ref. 243). It melts at 99°, boils at 212°, and is not affected when boiled with alkalies (see below).

β-**Chlorcrotonic Acid**, $CH_3.CCl:CH.CO_2H$, is obtained in small quantities (together with β-chlorisocrotonic acid) from aceto-acetic ester, and by the addition of HCl to tetrolic acid (*Berichte*, 22, Ref. 51). It melts at 94.5° and boils at 208°. Sodium amalgam reduces it to crotonic acid, and with boiling alkalies it yields tetrolic acid (p. 244). Sodium amalgam converts both α- and β-chlorcrotonic acid into ordinary crotonic acid.

α-**Bromcrotonic Acid**, from the ester of dibrombutyric acid, melts at 106.5°. β-**Bromcrotonic Acid**, formed by the addition of HBr to tetrolic acid, melts at 92° (*Berichte*, 22, Ref. 243).

(2) **Isocrotonic Acid**, $CH_2:CH.CH_2.CO_2H$(?), is obtained from β-chlorisocrotonic acid by the action of sodium amalgam and similarly from the α-chlor-acid. It is a liquid which does not solidify; boils at 172°, and has a specific gravity of 1.018 at 25°. When heated to 170°–180°, in a sealed tube, it changes to ordinary crotonic acid. This alteration occurs partially, even during distillation. This explains why upon fusing isocrotonic acid with KOH, formic and propionic acids (which might be expected), are not produced, but in their stead acetic acid, the decomposition product of crotonic acid. Sodium amalgam does not change it. It combines with HI to yield β-iodo-butyric acid (*Berichte*, 22, Ref. 741). It yields a liquid dichloride, $C_4H_6Cl_2O_2$ (Iso-αβ-dichlorbutyric acid), with Cl_2. This passes into α-chlorcrotonic acid. Sodium amalgam converts this acid into butyric acid.

α-**Chlor-isocrotonic Acid**, $CH_3.CH:CCl.CO_2H$ (?), is obtained by the action of sodium hydroxide on free αβ-dichlorbutyric acid. It is the most soluble of the four chlor-crotonic acids. It crystallizes in needles, melting at 66.5° (*Berichte*, 22, Ref. 52).

When PCl_5 and water act upon aceto-acetic ester, $CH_3.CO.CH_2.CO.C_2H_5$, β-chlorisocrotonic acid (with β-chlorcrotonic acid) is produced. It is very probable that β-dichlorbutyric acid is formed at first, and this afterwards parts with HCl. It is also formed by protracted heating of β-chlorcrotonic acid.

Sodium amalgam converts both the α- and β-chlorisocrotonic acid into liquid isocrotonic acid (*Berichte*, 22, Ref. 53).

α-**Bromisocrotonic Acid**, $CH_3.CH:CBr.CO_2H$ (?), is produced by the action of sodium hydroxide upon free αβ-dibrombutyric acid. It melts at 90°–92° (*Berichte*, 21, Ref. 242).

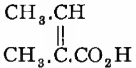
(3) **Methacrylic Acid,** $CH_2{:}C\left\langle\begin{matrix}CH_3\\CO_2H.\end{matrix}\right.$ Its ethyl ester was first obtained by the action of PCl_5 upon oxy-isobutyric ester, $(CH_3)_2.C(OH).CO_2.C_2H_5$. It is, however, best prepared by boiling citrabrom-pyrotartaric acid (from citraconic acid and HBr) with water or a sodium carbonate solution:—

$$C_5H_7BrO_4 = C_4H_6O_2 + CO_2 + HBr.$$

It consists of prisms that are readily soluble in water, fuse at +16°, and boil at 160.5°. NaHg converts the acid into isobutyric acid. It combines with HBr and HI to form α-brom-, and iod-isobutyric acid, and with bromine to form αβ-dibrom-isobutyric acid, which confirms the assumed constitution (*Journ. pr. Chemie*, 25, 369). When fused with KOH, it breaks up into propionic and acetic acids.

3. ACIDS OF FORMULA $C_5H_8O_2 = C_4H_7.CO_2H$.

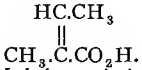
Of the many isomerides of this formula angelic and tiglic acids appear to bear the same relation to each other that was observed with crotonic and isocrotonic acids (p. 238). Both probably have the same structural formula (*Annalen*, 216, 161). According to Wislicenus they are only geometrical isomerides. They correspond to the stereochemical formulas:—



$$\begin{matrix}CH_3.CH\\ \|\\ CH_3.C.CO_2H\end{matrix}$$

α-Methyl-isocrotonic Acid.
Angelic Acid.

and



$$\begin{matrix}HC.CH_3\\ \|\\ CH_3.C.CO_2H.\end{matrix}$$

α-Methyl-crotonic Acid.
Tiglic Acid.

When fused with alkalies, both acids split up into acetic and propionic acids. They yield methyl-ethyl acetic acid when heated with HI and phosphorus. They form two different dibromides with bromine; these yield two different brombutylenes (*Annalen*, 250, 240).

1. **Angelic Acid,** $C_4H_7.CO_2H$, exists free along with valeric and acetic acids in the roots of *Angelica archangelica,* and as butyl and amyl esters in Roman oil of cumin.

To prepare the acid, boil the angelica roots with milk of lime, and distil the solution of the calcium salt with sulphuric acid. From the oily distillate, containing acetic, valeric and angelic acids, the latter crystallizes on cooling. The saponification of Roman cumin oil with potash, also furnishes the acid (*Annalen*, 250, 242).

Roman oil of cumin (from *Artemis nobilis*) contains the esters of several acids. The following fractions may be obtained from that portion of it which boils up to 210°:—

1. Isobutyl butyrate, boiling 147–148°.
2. " angelate, " 177–178°.
3. Amyl angelate, " 200–201°.
4. Amyl tiglate, " 204–205°.

When these esters are saponified and distilled with sulphuric acid, the free acids are obtained. We can separate angelic and tiglic acids by means of the calcium salts, that of the first being very readily soluble in cold water. (*Berichte*, 17, 2261).

Angelic acid crystallizes in shining prisms, melts at 45°, and boils at 185°. When boiled for some time it is converted into tiglic acid. Concentrated sulphuric acid at 100°, effects the same. The acid dissolves readily in hot water and alcohol. It is volatile with steam. Its *ethyl ester*, $C_5H_7O_2.C_2H_5$, boils at 141°.

2. *a*-**Methylcrotonic Acid,** $CH_3.CH:C\left\langle\begin{smallmatrix}CH_3\\CO_2H\end{smallmatrix}\right.$, (?) **Tiglic Acid,** present in Roman oil of cumin (see above), and in Croton oil (from *Croton tiglium*), is a mixture of glycerol esters of various fatty and oleic acids. It is obtained artificially by acting with PCl_3 upon methyl-ethyl oxy-acetic acid, $\left.\begin{smallmatrix}CH_3\\CH_3.CH_2\end{smallmatrix}\right\rangle C(OH).CO_2H$ (its ester), and from *a*-methyl-*β*-oxybutyric acid, $CH_3.CH(OH).CH(CH_3).CO_2H$, on heating the latter to 200° (*Annalen*, 250, 243).

Tiglic acid crystallizes in prisms or tables, is soluble with difficulty in water, melts at 64.5°, and boils at 198°. Its *ethyl ester*, $C_5H_7O_2.C_2H_5$, boils at 152°.

3. **Allyl-acetic Acid,** $CH_2:CH.CH_2.CH_2.CO_2H$, obtained from allyl-acetoacetate and allyl malonic acid (p. 235), is an oil, smelling like valeric acid, and boiling at 188°. Nitric acid oxidizes it to succinic acid. It unites with concentrated hydrobromic acid, and forms *γ*-bromvaleric acid (a non-solidifying oil), which, upon heating with water, parts with HBr and yields the lactone of *γ*-oxyvaleric acid (see Lactones).

4. **Propylidene Acetic Acid,** $CH_3.CH_2.CH:CH.CO_2H$, is obtained from propylidene malonic acid, $C_3H_5:C(CO_2H)_2$ (p. 235), and boils at 196° (*Annalen*, 218, 160). It has also been obtained from pyrocatechol and amidophenol (*Berichte*, 22, 495).

5. **Ethidene Propionic Acid,** $CH_3.CH:CH.CH_2.CO_2H$, is produced by the distillation of methyl paraconic acid, $C_6H_8O_4$. It is a liquid boiling at 104°. It unites with HBr to *γ*-bromvaleric acid, which readily passes into valerolactone (*Berichte*, 23, Ref. 91).

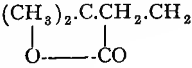
6. **Dimethyl Acrylic Acid,** $(CH_3)_2C:CH.CO_2H$, is obtained from *β*-oxyisovaleric acid, $(CH_3)_2.C(OH).CH_2.CO_2H$, by distillation with dilute sulphuric acid. It melts at 70°.

Tetramethylene carboxylic acid (see this) is isomeric with these unsaturated acids.

The following higher, unsaturated acids, may also be mentioned. Little is known concerning their constitution. They frequently sustain molecular transpositions:—

Pyroterebic Acid, $C_6H_{10}O_2 = (CH_3)_2.C:CH.CH_2.CO_2H$, is formed in small quantity (together with the isomeric lactone of *γ*-oxy-isocaproic acid) (see this), in the distillation of terebic acid, $C_7H_{10}O_4$ (*Annalen*, 208, 39 and 119). It is an oil which does not solidify at —15°. The *calcium salt*, $(C_6H_9O_2)_2Ca + 3H_2O$, crystallizes in shining prisms. Protracted boiling causes the free acid to change to isomeric isocaprolactone :—

$(CH_3)_2.C:CH.CH_2.CO_2H$ forms



$$\begin{array}{l}(CH_3)_2.C.CH_2.CH_2\\ \quad\;|\qquad\quad\;\;|\\ \quad\;O\text{———}CO\end{array};$$

concentrated hydrobromic acid effects the same change.

Teracrylic Acid, $C_7H_{12}O_2 = C_3H_7.CH:CH.CH_2.CO_2H$, is obtained by the distillation of terpentic acid, $C_8H_{12}O_4$ (see this), just as pyroterebic acid is formed from terebic acid. An oily liquid, with an odor resembling that of valeric acid, and boiling at 208° without decomposition. HBr converts it into the isomeric lactone of *γ*-oxyheptoic acid, $C_7H_{13}(OH)O_2$.

Nonylenic Acid, $C_9H_{16}O_2 = CH_3(CH_2)_5CH{:}CH.CO_2H$, is obtained from œnanthol (p. 198) by Perkins' reaction (p. 234). It is an oily liquid, which volatilizes with steam.

Decylenic Acid, $C_{10}H_{18}O_2$, formed together with decylacetone in the distillation of hexylparaconic acid (*Berichte*, 18, Ref. 144), solidifies in the cold and melts at + 10° C.

Undecylenic Acid, $C_{11}H_{20}O_2$, is produced by distilling castor oil under reduced pressure, when the ricinoleic acid, $C_{18}H_{34}O_3$ (p. 243), present as a glyceride, breaks up into œnanthol, $C_7H_{14}O$, and undecylenic acid. It melts at 24.5°, and boils with partial decomposition at 275°. It distils unchanged under reduced pressure. When fused with caustic potash, it splits up into acetic and nonoic acid, $C_9H_{18}O$. Hence its structure corresponds to the formula, $C_8H_{17}.CH{:}CH.CO_2H$ (compare *Berichte*, 19, Ref. 338, and 19, 2224).

Hypogæic Acid, $C_{16}H_{30}O_2$, found as glycerol ester in earthnut oil (from the fruit of *Arachis hypogæa*), crystallizes in needles, and melts at 33°. Nitrous acid converts it into an isomeric modification—*gaeïdinic acid*, melting at 38°.

Oleic Acid, $C_{18}H_{34}O_2$, occurs as glycerol ester (triolein) in nearly all fats, especially in the oils, as olive oil, almond oil, cod-liver oil, etc. It is obtained in large quantities as a by-product in the manufacture of stearin candles.

In preparing oleic acid, olive or mandel oil is saponified with potash and the aqueous solution of the potassium salts precipitated with sugar of lead. The lead salts which separate are dried and extracted with ether, when lead oleate dissolves, leaving as insoluble lead palmitate, stearate and the salts of all other fatty acids. Mix the ethereal solution with hydrochloric acid, filter off the lead chloride, and concentrate the liquid. To purify the acid obtained in this way, dissolve it in ammonium hydroxide, precipitate with barium chloride, crystallize the barium salt from alcohol, and decompose it away from the air by means of tartaric acid.

Oleic acid is a colorless oil, which crystallizes on cooling. It melts at + 14°. In a pure condition it is odorless, and does not redden litmus. On exposure to the air it oxidizes, becomes yellow and acquires a rancid odor. On fusion with caustic potash it splits up into palmitic and acetic acids. Nitric acid oxidizes it with formation of all the lower fatty acids from capric to acetic, and at the same time dibasic acids, like sebacic acid, are produced. A permanganate solution oxidizes it to azelaic acid, $C_9H_{16}O_4$. Moderated oxidation produces dioxystearic acid. The oleates are very similar to the salts of the fatty acids. Much water decomposes them. The solubility of the lead salt, $(C_{18}H_{33}O_2)_2Pb$, in ether is characteristic.

When heated to 200° with hydriodic acid and phosphorus, or with iodine (1 %) to 280°, oleic changes to stearic acid, $C_{18}H_{36}O_2$. It unites with bromine to form liquid dibromstearic acid, $C_{18}H_{34}Br_2O_2$, which is converted by alcoholic KOH into *monobromoleic acid*, $C_{18}H_{33}BrO_2$, and then into stearoleic acid.

Nitrous acid changes oleic into the isomeric crystalline

Elaïdic Acid, $C_{18}H_{34}O_2$. This consists of brilliant leaflets, melting at 44°–45°. If fused with potash it decomposes into propionic and acetic acids. Hydriodic acid and phosphorus convert it into stearic acid. With bromine it yields the bromide, $C_{18}H_{34}Br_2O_2$, which melts at 27°, and when acted upon with sodium amalgam, passes back into elaïdic acid.

Iso-oleic acid, obtained by the distillation of oxystearic acid, appears to be different from elaïdic acid. It also melts at 45° (*Berichte*, 21, Ref. 398; 21, 1879).

Erucic Acid, $C_{22}H_{42}O_2$, is present as glyceride in rape-seed oil (from *Brassica campestris*) and in the fatty oil of mustard. For its preparation, rape-seed oil is saponified with lead oxide, and the lead erucate removed with ether. Erucic acid crystallizes from alcohol in long needles, which melt at 33°–34°. It forms a *dibromide*, $C_{22}H_{42}Br_2O_2$, with bromine. This crystallizes in warty masses, melting at 42°, and when acted upon with alcoholic potash, changes to bromerucic acid, melting at 33°.

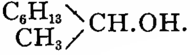
Hot nitric acid (*Berichte*, 19, 3321) converts erucic acid into isomeric *brassidic* acid, melting at 56°.

The *petrolic acids*, found in the different varieties of petroleum, are isomeric with the oleic acids. Up to the present time the following have been isolated: $C_{11}H_{20}O_2$, $C_{13}H_{24}O_2$ and $C_{15}H_{28}O_2$. In all probability they are the carboxylic acids of the naphthenes (p. 78) (*Berichte*, 20, 596; 23, 868).

Linoleic and ricinoleic acids, although not belonging to the same series, yet closely resemble oleic acid. The first is a simple, unsaturated acid, the second an unsaturated oxy-acid.

Linoleic Acid, $C_{18}H_{32}O_2$, occurs as glyceride in *drying oils* (see glycerol), such as linseed oil, hemp oil, poppy oil and nut oil. In the *non-drying* oils we have the oleic-glycerol ester. To prepare linoleic acid, saponify linseed oil with potash, precipitate the aqueous solution of the potassium salt with calcium chloride and dissolve out calcium linoleate with ether. Linoleic acid is a yellowish oil that has a specific gravity of 0.921. It is not altered by nitrous acid.

Various oxy-fatty acids are produced when linoleic acid is oxidized with potassium permanganate. From the fact that they can be formed it has been concluded that certain other acids (like linolenic and isolinolenic acid, $C_{18}H_{30}O_2$) exist in the crude linoleic acid (*Berichte*, 21, Ref. 436 and 659).

Ricinoleic Acid, $C_{18}H_{34}O_3$, is present in castor oil, in the form of a glyceride. It is a colorless oil, which solidifies in the cold to a hard, white mass, melting at 16–17°. The lead salt is soluble in ether. Subjected to dry distillation ricinoleic acid splits into œnanthol, $C_7H_{14}O$, and undecylenic acid, $C_{11}H_{20}O_2$. Fused with caustic potash it changes to sebacic acid, $C_8H_{16}(CO_2H)_2$, and secondary octyl alcohol,  $\begin{matrix}C_6H_{13}\\CH_3\end{matrix}\!\!>\!CH.OH$. It combines with bromine to a solid *dibromide*. When heated with HI (iodine and phosphorus) it is transformed into iodstearidic acid, $C_{18}H_{33}IO_2$, which yields stearic acid when treated with zinc and hydrochloric acid. Nitrous acid converts ricinoleic acid into isomeric *ricinelaïdic acid*. This melts at 53° C. (see *Berichte*, **21**, 2735).

UNSATURATED ACIDS, $C_nH_{2n-4}O_2$.

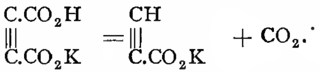
PROPIOLIC ACID SERIES.

The members of this series have four hydrogen atoms less than the normal acids. They can be obtained from the acids of the acrylic series by treating the halogen derivatives of the latter with alcoholic potash—just as the acetylenes are produced fom the olefines (see p. 87). Thus tetrolic acid, $C_4H_4O_2$, is obtained from the bromide of crotonic acid, $C_4H_6Br_2O_2$, and from bromcrotonic acid, $C_4H_5BrO_2$. They must be viewed as acetylene derivatives, formed by the replacement of one hydrogen atom by carboxyl; consequently they can be obtained by letting CO_2 act upon the sodium compounds of acetylene (p. 88):—

$$\underset{\text{Sodium Allylene.}}{CH_3.C\vdots CNa} + CO_2 = \underset{\text{Sodium Tetrolate.}}{CH_3.C\vdots C.CO_2Na.}$$

Like the acetylenes they are capable of directly binding 2 and 4 affinities. From their structure they may contain one triple union or two double unions of two carbon atoms (see p. 87).

Propiolic Acid, $C_3H_2O_2 = CH\vdots C.CO_2H$, **Propargylic Acid** (p. 135), corresponds to propargyl alcohol. The *potassium salt*, $C_3HKO_2 + H_2O$, is produced from the primary potassium salt of acetylene dicarboxylic acid, when its aqueous solution is heated:—



$$\begin{matrix} C.CO_2H \\ ||| \\ C.CO_2K \end{matrix} = \begin{matrix} CH \\ ||| \\ C.CO_2K \end{matrix} + CO_2.$$

Acetic acid results in like manner from malonic acid (p. 212).

The aqueous solution of the salt is precipitated by ammoniacal silver and cuprous chloride solutions, with formation of explosive metallic derivatives. By prolonged boiling with water the potassium salt is decomposed into acetylene and potassium carbonate.

Free propiolic acid, liberated from the potassium salt, is a liquid with an odor resembling that of glacial acetic acid. When cool it solidifies to silky needles which melt at + 6°. The acid dissolves readily in water, alcohol and ether, boils with decomposition at 144° and reduces silver and platinum salts. Exposed to sunlight (away from air contact) it polymerizes to trimesinic acid, $3C_2H.CO_2H = C_6H_3(CO_2H)_3$. Sodium amalgam converts it into propionic acid. It forms β-halogen acrylic acids with the halogen acids (p. 237) (*Berichte*, **19**, 543).

The *ethyl ester*, $C_3HO_2.C_2H_5$, is formed on digesting the acid with alcohol and sulphuric acid. It boils at 119°. With ammoniacal cuprous chloride it unites to a stable yellow-colored compound. Zinc and sulphuric acid reduce it to ethyl propargylic ester (p. 135) (*Berichte*, 18, 2271).

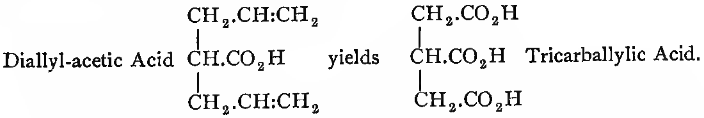
Chlorpropiolic Acid, C_3HClO_2, and **Brompropiolic Acid**, C_3BrHO_2, have been obtained as barium salts from dichloracrylic and mucobromic acids, $C_3H_2Cl_2O_2$ and $C_4H_2Br_2O_3$. They are readily decomposed with evolution of chlor- and brom-acetylene. **Iodopropiolic Acid**, $C_3HIO_2 = CI\vdots C.CO_2H$, is obtained by saponifying its ethyl ester with NaOH. It crystallizes from ether in small prisms, melting at 140°. On warming its alkali salts with water carbonates and iodoacetylene are produced. The acid combines with iodine to form tri-iodo-acrylic acid, $C_3HI_3O_2$ (*Berichte*, 18, 2274 and 2282). The ethyl ester, $C_3IO_2.C_2H_5$, may be prepared from the Cu- derivative of propiolic ester (see above) by the action of iodine. It crystallizes from ether in large prisms, melting at 68°. What is remarkable about this compound is the stable union of the iodine contained in it (*Berichte*, 19, 540).

Tetrolic Acid, $C_4H_4O_2 = CH_3.C\vdots C.CO_2H$, is obtained from β-chlorcrotonic acid and β-chlorisocrotonic acid (p. 239) when these are boiled with potash (*Annalen*, 219, 346); from sodium allylene by the action of CO_2 (see above), and from the chloride of allylene by means of Na and CO_2. The acid consists of tables, very readily soluble in water, alcohol and ether. It melts at 76° and boils at 203°. At 210° the acid decomposes into CO_2 and allylene, C_3H_4. Potassium permanganate oxidizes it to acetic and oxalic acids. It combines with HCl and forms β-chlorcrotonic acid.

Propyl-acetylene Carbonic Acid, $C_3H_7.C\vdots C.CO_2H$, from propylacetylene sodium, $C_3H_7.C\vdots CNa$, melts at 27°. **Isopropyl-acetylene Carbonic Acid**, from isopropyl acetylene, melts at 38° (*Berichte*, 21, Ref. 178).

Sorbic Acid, $C_6H_8O_2 = C_5H_7.CO_2H$, occurs together with malic acid in the juice of unripe mountain-ash berries (from *Sorbis aucuparia*). Liberated from its salts by distillation with sulphuric acid (*Annalen*, 110, 129) it is an oil which does not solidify until after it has been heated with potash. In cold water it is almost insoluble, but crystallizes from alcohol in long needles, melting at 134.5°, and distilling at 228° without decomposition. It combines with bromine and yields the bromides, $C_8H_8Br_2O_2$ and $C_6H_8Br_4O_2$—the first melting at 95° and the second at 183°. The *ethyl ester* boils at 195°. Nascent hydrogen converts the acid into *hydrosorbic acid*, $C_6H_{10}O_2$. This possesses an odor like that of perspiration, boils at 208°, and, when fused with KOH, yields acetic and butyric acids.

Diallylacetic Acid, $C_8H_{12}O_2 = (C_3H_5)_2.CH.CO_2H$, is obtained from ethyl diallyl-aceto-acetate and diallyl malonic acid. It is a liquid, boiling at 221°. Nitric acid oxidizes it to tricarballylic acid:—



$$\begin{array}{lllll} & CH_2.CH{:}CH_2 & & CH_2.CO_2H & \\ & | & & | & \\ \text{Diallyl-acetic Acid} & CH.CO_2H & \text{yields} & CH.CO_2H & \text{Tricarballylic Acid.} \\ & | & & | & \\ & CH_2.CH{:}CH_2 & & CH_2.CO_2H & \end{array}$$

Undecolic Acid, $C_{11}H_{18}O_2$, is obtained from the bromide of undecylenic acid (p. 242). It fuses at 59.5°. **Palmitolic Acid**, $C_{16}H_{28}O_2$, isomeric with linoleic acid (p. 243), is obtained from the bromide of hypogæic acid and gæïdinic acid (p. 242). It melts at 42°. **Stearoleic Acid**, $C_{18}H_{32}O_2$, is obtained from oleic and elaïdic acids. It melts at 48°. **Behenolic Acid**, $C_{22}H_{40}O_2$, from the bromides of erucic and brassidic acids, melts at 57.5°. On warming the last three acids with fuming nitric acid they absorb 3 atoms of oxygen in a very peculiar manner, and yield the monobasic acids: *palmitoxylic*, $C_{18}H_{28}O_4$, *stearoxylic*, $C_{18}H_{32}O_4$, and *behenoxylic*, $C_{22}H_{40}O_4$, which melt at 67°, 86° and 96°, respectively.

DERIVATIVES OF THE ACIDS.

1. THE ACID HALOIDS.

The haloid anhydrides of the acids (or acid haloids) are those derivatives which arise in the replacement of the hydroxyl of acids by halogens; they are the halogen compounds of the acid radicals (p. 213). Their most common method of formation consists in letting the phosphorus haloids act upon the acids or their salts—just as the alkylogens are produced from the alcohols (p. 92).

(1) At ordinary temperatures phosphorus pentachloride acts very energetically upon the acids:—

$$C_2H_3O.OH + PCl_5 = C_2H_3O.Cl + POCl_3 + HCl.$$

The product of the reaction is subjected to fractional distillation. It is better to have PCl_3 act upon the alkali salts or the free acids; heat is then not necessary:—

$$3C_2H_3O.OK + PCl_3 = 3C_2H_3O.Cl + PO_3K_3.$$

By this method the pure acid chloride is at once obtained in the distillate—while the phosphite remains as residue. Or, phosphorus oxychloride (1 molecule) may be permitted to act on the dry alkali salt (2 molecules) when a metaphosphate will remain:—

$$2C_2H_3O.ONa + POCl_3 = 2C_2H_3O.Cl + PO_3Na + NaCl.$$

Should there be an excess of the salt, the acid will also act upon it and acid anhydrides result (p. 248).

Phosphorus bromides behave similarly. A mixture of amorphous phosphorus and bromine may be employed as a substitute for the prepared bromide (p. 95). Phosphorus iodide will not convert the acids into iodides of the acid radicals; this only occurs when the acid anhydrides are employed.

(2) Carbon oxychloride acts upon the free acids and their salts the same as the chlorides of phosphorus. Acid chlorides and anhydrides are produced. This method has met with technical application (*Berichte*, 17, 1285; 21, 1267):—

$$C_2H_3O.OH + COCl_2 = C_2H_3OCl + CO_2 + HCl.$$

(3) An interesting method for preparing the acid bromides consists in letting air act upon certain bromide derivatives of the alkylens, whereby oxygen will be absorbed. Thus, from $CBr_2{:}CH_2$ we obtain bromacetyl bromide, $CH_2Br.COBr$; from $CBr_2{:}CHBr$, dibromacetyl bromide, $CBr_2H.COBr$ (p. 97 and *Berichte*, 13, 1980; 21, 3356).

The acid haloids are sharp-smelling liquids, which fume in the air, because of their transformation into acids and halogen hydrides. They are heavier than water, sink in it, and at ordinary temperatures decompose, forming acids:—

$$C_2H_3O.Cl + H_2O = C_2H_3O.OH + HCl.$$

The more readily soluble the resulting acid is in water, the more energetic will the reaction be.

The acid chlorides act similarly upon many other bodies. They yield compound ethers, or esters, with the alcohols or alcoholates (p. 251). With salts or acids they yield acid anhydrides (p. 248), and with ammonia, the amides of the acids, etc.

Sodium amalgam, or better, sodium and alcohol, will convert the acid chlorides into aldehydes and alcohols (pp. 122 and 188). They yield ketones and tertiary alcohols when treated with the zinc alkyls (pp. 200 and 120).

Acetyl Chloride, $C_2H_3OCl = CH_3.CO.Cl$, is produced also by the action of hydrogen chloride and phosphorus pentoxide upon acetic acid, and when chlorine acts on aldehyde. It is a colorless, pungent-smelling liquid which boils at 55°, and has a specific gravity of 1.130 at 0°. Water decomposes it very energetically.

Preparation.—Bring PCl_5 into a retort with a tubulure, and through the latter gradually add anhydrous acetic acid. After the first violent action, apply heat and fractionate the distillate. It would be better to distil carefully a mixture of acetic acid (3 parts) and PCl_3 (2 parts). Or, heat $POCl_3$ (2 molecules) with acetic acid (3 molecules), as long as HCl escapes, then distil (*Annalen*, 175, 378). The acetyl chloride is purified by again distilling over a little dry sodium acetate.

Acetyl chloride forms the following substitution products with chlorine: $C_2H_2ClO.Cl$, boiling at 106°; $C_2HCl_2O.Cl$ and $C_2Cl_3O.Cl$; the latter boil at 118°. These are also obtained when phosphorus chloride acts on the substituted acetic acids. Monobromacetyl chloride, $C_2H_2BrO.Cl$, boils at 134°.

Acetyl Bromide, $C_2H_3O.Br$, boils at 81° and forms substitution products with bromine. **Monochloracetyl Bromide,** $C_2H_2ClO.Br$, from monochloracetic acid, boils at 134°.

Acetyl Iodide, $C_2H_3O.I$, is obtained by letting I and P act upon acetic anhydride. It boils at 108° and is colored brown by separated iodine.

Propionyl Chloride, $CH_3.CH_2.CO.Cl$, boils at 80°; the *bromide*, $C_3H_5O.Br$, at 97°, and the *iodide*, $C_3H_5O.I$, at 127°.

Butyryl Chloride, $C_4H_7O.Cl$, from normal butyric acid, boils at 101°. Sodium amalgam converts it into normal butyl alcohol. **Isobutyryl Chloride,** $(CH_3)_2.CH.CO.Cl$, boils at 92°.

Isovaleryl Chloride, $C_5H_9O.Cl$, from isovaleric acid, boils at 115°.

2. ACID CYANIDES.

When the chlorides of the acid radicals are heated with silver cyanide, *cyanides of the acid radicals*, like acetyl cyanide, $CH_3.CO.CN$, result. They can also be obtained by the action of dehydrating agents, *e. g.*, acetic anhydride upon isonitrosoketones (*Berichte*, 20, 2196):—

$$CH_3.CO.CH{:}N.OH = CH_3.CO.CN + H_2O.$$

Water or alkalies will readily convert these into their corresponding acids and hydrogen cyanide, $CH_3.CO.CN + H_2O = CH_3.CO.OH + CNH$. With concentrated hydrochloric acid, on the contrary, they sustain a transposition similar to that of the alkyl cyanides (p. 211), *i. e.*, carboxyl derivatives of the acid radicals—the so-called α-ketonic acids (see these)—are produced:—

$$CH_3.CO.CN + 2H_2O + HCl = CH_3.CO.CO_2H + NH_4Cl.$$

Acetyl Cyanide, $CH_3.CO.CN$, boils at 93°. When preserved for some time, or by the action of KOH or sodium, it is transformed into a polymeric, crystalline compound, $(C_2H_3OCN)_2$, diacetyl cyanide. This melts at 69° and boils at 208°. Concentrated hydrochloric acid converts it into pyroracemic acid.

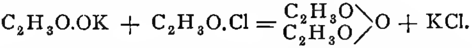
Diacetyl cyanide is also produced by the action of potassium cyanide upon acetic anhydride (*Berichte*, 18, 256).

Propionyl Cyanide, $CH_3.CH_2.CO.CN$, from propionyl chloride, boils at 108–110°. **Dipropionyl Cyanide**, $(C_3H_5O.CN)_2$, formed by the action of silver cyanide upon propionyl bromide, melts at 59°, and boils at 200–210° (*Berichte*, 18, Ref. 140). **Butyryl Cyanide**, $C_3H_7.CO.CN$, boils at 133–137°; isobutyryl cyanide, $C_3H_7.CO.CN$, at 118–120°. These polymerize readily to dicyanides.

3. ACID ANHYDRIDES AND PEROXIDES.

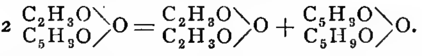
The acid anhydrides are the oxides of the acid radicals. In those of the monobasic acids two acid radicals are united by an oxygen atom; they are analogous to the oxides of the monovalent alcohol radicals—the ethers. They cannot, however, be made by the direct withdrawal of water from the acids. Anhydrides do indeed result by the action of P_2O_5, but their quantity is very small. The following methods are employed in their preparation:—

(1) The chlorides of the acid radicals are allowed to act on anhydrous salts, viz., the alkali salts of the acids:—



$$C_2H_3O.OK + C_2H_3O.Cl = \begin{matrix}C_2H_3O\\ C_2H_3O\end{matrix}\!\!>\!O + KCl.$$

The *simple* anhydrides, those containing two *similar* radicals, can as a general thing be distilled, while the *mixed* anhydrides, with two dissimilar radicals, decompose when thus treated, into two simple anhydrides:—



$$2\begin{matrix}C_2H_3O\\ C_5H_9O\end{matrix}\!\!>\!O = \begin{matrix}C_2H_3O\\ C_2H_3O\end{matrix}\!\!>\!O + \begin{matrix}C_5H_9O\\ C_5H_9O\end{matrix}\!\!>\!O.$$

Hence they are not separated from the product of the reaction by distillation, but are dissolved out with ether.

A direct conversion of the acid chlorides into the corresponding anhydrides may be effected by permitting the former to act upon anhydrous oxalic acid (*Annalen*, 226, 14):—

$$2C_2H_3OCl + C_2O_4H_2 = (C_2H_3O_2)O + 2HCl + CO_2 + CO.$$

(2) Phosphorus oxychloride (1 molecule) acts upon the dry alkali salts of the acids (4 molecules). The reaction is essentially

the same as the first. The acid chloride which appears in the beginning acts immediately upon the excess of salt:—

$$2C_2H_3O.OK + POCl_3 = 2C_2H_3O.Cl + PO_3K + KCl, \text{ and}$$
$$C_2H_3O.OK + C_2H_3O.Cl = (C_2H_3O)_2O + KCl.$$

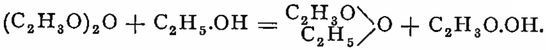
Phosgene, $COCl_2$, acts like $POCl_3$. In this reaction acid chlorides are also produced.

The anhydrides of the fatty acids can be produced further by the action of acetyl chloride on the latter (*Berichte*, 10, 1881).

The acid anhydrides are liquids or solids of neutral reaction, and are soluble in ether. Water decomposes them into their constituent acids:—

$$(C_2H_3O)_2O + H_2O = 2C_2H_3O.OH.$$

With alcohols they yield the acid esters (p. 251):—



$$(C_2H_3O)_2O + C_2H_5.OH = \begin{matrix} C_2H_3O \\ C_2H_5 \end{matrix}\!\!>\!O + C_2H_3O.OH.$$

Chlorine splits them up into acid chlorides and chlorinated acids:—

$$(C_2H_3O)_2O + Cl_2 = C_2H_3O.Cl + C_2H_3ClO.OH.$$

Heated with hydrochloric acid they decompose into an acid chloride and free acid:—

$$(C_2H_3O)_2O + HCl = C_2H_3O.Cl + C_2H_3O.OH.$$

HBr and HI act similarly. As the *heat modulus* is positive in this reaction, the reverse reaction (action of acid chloride upon the acid) is generally not adapted to the formation of anhydrides (compare *Annalen*, 226, 5).

Acetic Anhydride—Acetyl Oxide, $(C_2H_3O)_2O$, is a mobile liquid boiling at 137°. Its specific gravity equals 1.073 at 0°.

To prepare it, distil a mixture of anhydrous sodium acetate (3 parts) with phosphorus oxychloride (1 part); or, better, employ equal quantities of the salt and acetyl chloride. The distillate is redistilled over sodium acetate, to entirely free it from chloride.

Nascent hydrogen converts it first into aldehyde and then into alcohol (p. 188).

Propionic Anhydride or Propionyl Oxide, $(C_3H_5O)_2O$, boils at 168°. **Butyric Anhydride**, $(C_4H_7O)_2$, boils near 190°; its specific gravity = 0.978 at

12.5°. **Isovaleric Anhydride**, $(C_5H_9O)_2O$, boils with partial decomposition about 215°. Its specific gravity at 15° equals 0.934. It possesses an odor like that of apples.

The higher anhydrides do not volatilize without undergoing decomposition. **Caprylic Anhydride**, $(C_8H_{15}O)_2O$, melts at 0°. **Myristic Anhydride**, $(C_{14}H_{27}O)_2O$, forms a fatty mass, fusing at 54°.

The peroxides of the acid radicals are produced on digesting the chlorides or anhydrides in ethereal solution with barium peroxide:—

$$2C_2H_3O.Cl + BaO_2 = (C_2H_3O)_2O_2 + BaCl_2.$$

Acetyl Peroxide is a thick liquid, insoluble in water, but readily dissolved by alcohol and ether. It is a powerful oxidizing agent, separating iodine from potassium iodide solutions, and decolorizing a solution of indigo. Sunlight decomposes it, and when heated it explodes violently. With barium hydroxide it yields barium acetate and barium peroxide.

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4. THIO-ACIDS AND THIO-ANHYDRIDES.

The thio-acids, *e.g.*, thio-acetic acid, $CH_3.CO.SH$, correspond to the thio-alcohols or mercaptans (p. 140), and are produced by analogous methods: by the action of acid chlorides upon potassium sulphydrate, KSH, and by heating acids with phosphorus pentasulphide:—

$$5C_2H_3O.OH + P_2S_5 = 5C_2H_3O.SH + P_2O_5.$$

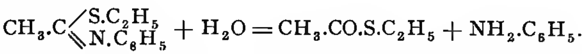
The *thio-anhydrides* arise in the same manner by the action of phosphorus sulphide upon the acid anhydrides.

The thio-acids are disagreeably-smelling liquids, more insoluble in water and possessing lower boiling temperatures than the corresponding oxygen acids. Like the latter, they yield salts and esters. When heated with dilute mineral acids they break up into H_2S and fatty acids. Water slowly decomposes the thio-anhydrides into a thio-acid and an oxy-acid.

The *esters* are obtained when the alkylogens react with the salts of the thio-acids, and by letting the acid chlorides act upon the mercaptans or mercaptides:—

$$C_2H_3O.Cl + C_2H_5.SNa = C_2H_3O.S.C_2H_5 + NaCl.$$

They also appear in the decomposition of alkylic isothio-acetanilides with dilute hydrochloric acid:—



$$CH_3.C\begin{matrix}\diagup S.C_2H_5 \\ \diagdown\!\!\diagdown N.C_6H_5\end{matrix} + H_2O = CH_3.CO.S.C_2H_5 + NH_2.C_6H_5.$$

Ethyl-isothio-acetanilide. Thioacetic Ester. Aniline.

Concentrated potash resolves the esters into fatty acids and mercaptans.

Thiacetic Acid, $C_2H_3O.SH$, is a colorless liquid, boiling at 93°, and having a specific gravity of 1.074 at 10°. Its odor resembles that of acetic acid and hydrogen sulphide. It is sparingly soluble in water, but dissolves readily in alcohol and ether. The *lead salt,* $(C_2H_3O.S)_2Pb$, crystallizes in delicate needles, and readily decomposes with formation of lead sulphide. **Ethyl Thiacetate,** $C_2H_3O.S.C_2H_5$, boils at 115°.

Acetyl Sulphide, $(C_2H_3O)_2S$, is a heavy, yellow liquid, insoluble in water; and is slowly decomposed by this liquid into acetic acid and thiacetic acid. It boils at 121°.

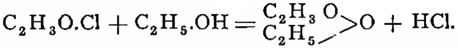
Acetyl Disulphide, $(C_2H_3O)_2S_2$, is produced when acetyl chloride acts upon potassium disulphide, or iodine upon salts of the thio-acids:—

$$2C_2H_3O.SNa + I_2 = (C_2H_3O)_2S_2 + 2NaI.$$

5. ESTERS OF THE FATTY ACIDS.

The esters of organic acids resemble those of the mineral acids in all respects (p. 146), and are prepared by analogous methods:—

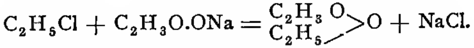
(1) By the action of acid chlorides (or acid anhydrides, p. 246) on the alcohols or alcoholates:—



$$C_2H_3O.Cl + C_2H_5.OH = \left.\begin{matrix}C_2H_3O\\C_2H_5\end{matrix}\right>O + HCl.$$

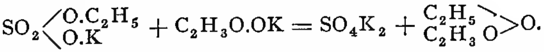
Transpositions frequently occur when alcoholates are used, for example, when ethyl ester is converted into a methyl ester by the action of methyl sodium. It is also true in the reverse case (*Berichte,* 20, 1554).

(2) By the action of the alkylogens upon salts of the acids:—



$$C_2H_5Cl + C_2H_3O.ONa = \left.\begin{matrix}C_2H_3O\\C_2H_5\end{matrix}\right>O + NaCl.$$

(3) By the dry distillation of a mixture of the alkali salts of the fatty acids and salts of alkyl sulphates (p. 149):—



$$SO_2\left<\begin{matrix}O.C_2H_5\\O.K\end{matrix}\right. + C_2H_3O.OK = SO_4K_2 + \left.\begin{matrix}C_2H_5\\C_2H_3O\end{matrix}\right>O.$$

(4) By direct action of acids and alcohols, whereby water is formed at the same time:—

$$C_2H_5.OH + C_2H_3O.OH = C_2H_5.O.C_2H_3O + H_2O.$$

This transposition, as already stated, only takes place slowly (p. 147); heat hastens it, but it is never complete. If a mixture of like equivalents of alcohol and acid be employed, there will occur a time in the action when a condition of equilibrium will prevail, when the ester formation will cease, and both acid and alcohol will be simultaneously present in the mixture. This ensues, because the heat modulus of the reaction is very slight, and hence, in accordance with the principles of thermo-chemistry, and under slightly modified conditions, the reaction pursues a reverse course, *i. e.*, the ester is decomposed by more water into alcohol and acid, since heat is generated when they are dissolved by the water. Both reactions mutually limit themselves. With excess of alcohol, more acid can be changed to ester, and with excess of acid more alcohol. The formation of the esters is more complete and rapid, if the reaction products are assiduously withdrawn from the mixture. This may be effected either by distillation (providing the ester is readily volatilized), or by combining the water formed with sulphuric or hydrochloric acid, when the heat modulus will be appreciably augmented.* We practically have from the above the following methods of preparation. Distil the mixture of the acid or its salt with alcohol and sulphuric acid. Or, when the esters volatilize with difficulty, the acid or its salt is dissolved in excess of alcohol (or the alcohol in the acid), and while applying heat, HCl gas is conducted into the mixture (or H_2SO_4 added), and the ester precipitated by the addition of water. The acid nitriles can be directly converted into esters, by dissolving them in alcohol, and heating them with dilute sulphuric acid (p. 211).

Berthelot has executed more extended investigations upon the *ester* formation. These are of great importance to chemical dynamics. He observed, for instance, that the reaction is materially accelerated by heat, but that a limit to the ester production invariably occurs, and that it equals that of the reverse transposition of the esters by water. This limiting point is independent of the speed of the reaction and temperature, but is controlled by the relative quantities, as well as the nature of the alcohol and acid. According to Berthelot the speed of the ester formation in the case of the primary normal alcohols is almost the same; the degree of the conversion or transposition equals about 66 per cent. of the mixture (with equivalent quantities of alcohol and acid). Proceeding from the simple assumption that the quantities of alcohol and acid combining in a unit of time (speed of reaction) are proportional to the product of the reacting masses, whose quantity regularly diminishes, Berthelot has proposed a formula (*Annalen chim. phis.*, 1862) by which the speed of the reaction in every moment of time, and its extent, can be calculated. van't Hoff has deduced a similar formula (*Berichte*, 10, 669), which Guldberg-Waage and Thomsen pronounce available for all limited reactions (*ibid*, 10, 1023). For a tabulation of the various calculations relating to this matter, see *Berichte*, 17, 2177; 19, 1700. Of late Menschutkin has extended the investigations upon ester formations to the several homologous series of acids and alcohols (*Annalen*, 195, 334 and 197, 193; *Berichte*, 15, 1445 and 1572; 21, Ref. 41).

Usually the esters of fatty acids are volatile, neutral liquids, soluble in alcohol and ether, but generally insoluble in water. Heated with the latter they sustain a partial decomposition into alcohol and

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* Consult *Annalen*, 211, 208.

acid. This decomposition (*saponification*) is more rapid and complete on heating with alkalies in alcoholic solution:—

$$C_2H_3O.O.C_2H_5 + KOH = C_2H_3O.OK + C_2H_5.OH.$$

Consult *Annalen*, 228, 257, and 232, 103; *Berichte*, 20, 1634, upon the velocity of saponification by various bases.

Ammonia changes the esters into amides (p. 256):—

$$C_2H_3O.O.C_2H_5 + NH_3 = C_2H_3.O.NH_2 + C_2H_5.OH.$$

The haloid acids convert the esters into acids and haloid-esters (*Annalen*, 211, 178):—

$$C_2H_3O.O.C_2H_5 + HI = C_2H_3O.OH + C_2H_5I.$$

PCl_5 introduces chlorine, and the radicals are converted into halogen derivatives:—

$$C_2H_3O.O.C_2H_5 + PCl_5 = C_2H_3O.Cl + C_2H_5Cl + POCl_3.$$

The esters of the fatty acids possess an agreeable fruity odor, are prepared in large quantities, and find extended application as *artificial fruit essences.* Nearly all fruit-odors may be made by mixing the different esters. The esters of the higher fatty acids occur in the natural varieties of wax.*

ESTERS OF FORMIC ACID.

Methyl Formic Ester, $CHO_2.CH_3$, is obtained by distilling sodium formate with sodium methyl sulphate, or more advantageously by adding methyl alcohol (13 parts) saturated with HCl-gas to calcium formate (10 parts) and then distilling. Another course consists in conducting HCl into a mixture of formic acid and alcohol, and then distilling. A mobile, agreeably-smelling liquid, that boils at 32.5° and has a specific gravity of 0.9984 at 0°. In sunlight chlorine produces **Perchlor-methyl formic ester**, $CClO_2.CCl_3$, which boils at 180–185°. Heated to 305° it breaks up into carbonyl chloride, $C_2Cl_4O_2 = 2COCl_2$. Aluminium chloride converts it into CCl_4 and CO_2.

Ethyl Formic Ester, $CHO_2.C_2H_5$, boils at 54.4° and dissolves in 10 parts water. Its specific gravity equals 0.9445. To prepare it, distil a mixture of dry sodium formate (7 parts), sulphuric acid (10 parts), and 90 per cent. alcohol (6 parts). It is better to heat a mixture of oxalic acid, glycerol and alcohol in a flask with a return cooler, until the evolution of carbon dioxide ceases, then distil off the ester; at first a glycerol ester of formic acid is produced (p. 217), which the alcohol decomposes.

The above *ester* serves in the manufacture of artificial rum and arrack.

The *propyl ester*, $CHO_2.C_3H_7$, boils at 81°. The *butyl ester*, $CHO_2.C_4H_9$, boils at 107°. The normal *amyl ester* boils at 130.4°. *Isoamyl ester*, $CHO_2.C_5H_{11}$, has a fruity odor and boils at 123°.

The *allyl ester*, $CHO_2.C_3H_5$, is formed on heating oxalic acid with glycerol, and boils at 82–83° (p. 134).

For higher esters consult *Annalen*, 233, 253.

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* Ueber die Siedepunkte der Fettsäureester und ihre spec. Gewichte s. *Berichte*, 14, 1274 u. *Annalen*, 218, 337. Ueber die specif. Volumen. s. *Annalen*, 220, 290 u. 319; *Annalen*, 223, 249.

ESTERS OF ACETIC ACID.

The **Methyl Ester**, Methyl Acetate, $C_2H_3O_2.CH_3$, occurs in crude wood-spirit, boils at 57.5°, and has a specific gravity of 0.9577 at 0°. When chlorine acts upon it the alcohol radical is first substituted: $C_2H_3O_2.CH_2Cl$ boils at 150°; $C_2H_3O_2.CHCl_2$ boils at 148°.

The **Ethyl Ester**, Ethyl Acetate—Acetic Ether—$C_2H_3O_2.C_2H_5$, is a liquid with refreshing odor, and boils at 77°. At 0° its sp. gr. equals 0.9238. It dissolves in 14 parts water, and readily decomposes into acetic acid and alcohol. In preparing it, heat a mixture of 100 c.c. H_2SO_4 and 100 c c. alcohol to 140°, and gradually run in a mixture of 1 litre alcohol (95°) and 1 litre acetic acid (*Berichte*, **16**, 1227). The distillate is shaken with a concentrated solution of salt, to withdraw all alcohol, the ether is siphoned off, dehydrated over calcium chloride, and finally rectified.

Chlorine produces substitution products of the alcohol radicals. Sodium dissolves in the anhydrous ester, forming sodium aceto-acetic ester. The *propyl ester*, $C_2H_3O_2.C_3H_7$, boils at 101°; sp. gr. 0.9091 at 0°. The *isopropyl ester* boils at 91°.

The *butyl ester*, $C_2H_3O_2.C_4H_9$, is obtained from normal butyl alcohol. It boils at 124°. The ester of primary isobutyl alcohol boils at 116°; that of the secondary alcohol at 111°, and that of the tertiary at 96°.

Amyl Esters, $C_2H_3O_2.C_5H_{11}$. The ester of normal amyl alcohol boils at 148°; that of propyl-methyl carbinol at 133°, and that of isopropyl methyl carbinol at 125°. At 200° it splits up into amylene and acetic acid. The acetic ester of amyl alcohol of fermentation (p. 130) boils at 140°. A dilute alcoholic solution of it has the odor of pears and is used as *pear oil*.

Hexyl acetic ester, $C_2H_3O_2.C_6H_{13}$, with the normal hexyl group, occurs in the oil of *Heracleum giganteum*. It boils at 169–170° and possesses a fruit-like odor. The *octyl ester*, $C_2H_3O_2.C_8H_{17}$, is also present in the oil of *Heracleum giganteum*. It boils at 207° and has the odor of oranges.

The *allyl-ester*, $C_2H_3O.O.C_3H_5$, obtained from allyl iodide, boils at 98–100°.

Consult *Annalen*, 233, 260 for higher acetic acid esters.

ESTERS OF PROPIONIC ACID.

The *methyl ester*, $C_3H_5O_2.CH_3$, boils at 79.5°. The *ethyl ester*, $C_3H_5O_2.C_2H_5$, boils at 98°. The *propyl ester*, $C_3H_5O_2.C_3H_7$, boils at 122°; the *isobutyl ester*, $C_3H_5O_2.C_4H_9$, at 137°; and the *isoamyl ester*, $C_3H_5O_2.C_5H_{11}$, at 160°; the latter has an odor like that of pine-apples. (See *Annalen*, 233, 265.)

ESTERS OF THE BUTYRIC ACIDS.

Methyl Butyric Ester, $C_4H_7O_2.CH_3$, boils at 102.3°. The *ethyl ester*, $C_4H_7O_2.C_2H_5$, boils at 120.9°, has a pine-apple-like odor, and is employed in the manufacture of artificial rum. Its alcoholic solution is the artificial *pine-apple oil*. This is prepared on a large scale by saponifying butter with sodium hydroxide and distilling the sodium salt which is formed with alcohol and sulphuric acid.

The *normal propyl ester*, $C_4H_7O_2.C_3H_7$, boils at 143°; the *isopropyl ester*, $C_4H_7O_2.C_3H_7$, at 128°. The *isobutyl ester*, $C_4H_7O_2.C_4H_9$, boils at 157°. The *isoamyl ester*, $C_4H_7O_2.C_5H_{11}$, boils at 178°, and its odor resembles that of pears. The *hexyl ester* and *octyl ester* are found in the oil obtained from various species of *Heracleum* (see above). See, also, *Annalen*, 233, 271.

Ethyl Isobutyric Ester, $C_4H_7O_2.C_2H_5$, boils at 110°.

The *esters* of the higher acids, as well as those of the substituted acids, are mostly mentioned along with the latter. We may yet notice here:—

Isoamyl Isovaleric Ester, $C_5H_9O_2.C_5H_{11}$, boils at 196°, and is obtained by direct oxidation of the amyl alcohol of fermentation. Its odor is very much like that of apples, and it finds application under the name *apple oil.*

See *Annalen* 233, 273–290, for esters of hexoic, heptoic, valeric and octoic acids.

The complex esters, having high molecular weights, are solids, and cannot be distilled without suffering decomposition. Thus *cetyl acetic ester*, $C_2H_3O_2.C_{16}H_{33}$, melts at 18.5°; *ethyl palmitic ester*, $C_{16}H_{31}O_2.C_2H_5$, at 24°. These esters are prepared by dissolving the acid in alcohol, or the latter in the acid, and then saturating the solution with HCl (p. 252). The *esters* with high alkyls break up into olefines and fatty acids (p. 80) when distilled under pressure.

Some of the higher esters occur already formed in waxes and in spermaceti.

Spermaceti (*Cetaceum, Sperma Ceti*) occurs in the oil from peculiar cavities in the head of whales (particularly *Physeter macrocephalus*), and upon standing and cooling it separates as a white crystalline mass, which can be purified by pressing and recrystallization from alcohol. It consists of **Cetyl Palmitic Ester**, $C_{16}H_{31}O_2.C_{16}H_{33}$, which crystallizes from hot alcohol in waxy, shining needles or leaflets, and melts at 49°. It volatilizes undecomposed in a vacuum. Distilled under pressure, it yields hexadecylene and palmitic acid. When boiled with caustic potash it becomes palmitic acid and cetyl alcohol.

Chinese wax is **Ceryl Cerotic Ester**, $C_{27}H_{53}O_2.C_{27}H_{55}$. Alcoholic potash decomposes it into cerotic acid and ceryl alcohol.

Ordinary beeswax is a mixture of cerotic acid, $C_{27}H_{54}O_2$, with **Myricyl Palmitic Ester**, $C_{16}H_{31}O_2.C_{30}H_{61}$. Boiling alcohol extracts the cerotic acid and the ester remains. *Annalen*, 224, 225.

Beeswax further contains the two hydrocarbons *Heptacosane*, $C_{27}H_{56}$, and *Hentriacontane*, $C_{31}H_{64}$, in addition to several alcohols, from $C_{25}H_{52}O$ to $C_{31}H_{64}O$ (*Annalen*, 235, 106).

Carnäuba wax, from the leaves of the carnuba tree, melts at 83°. It contains free ceryl alcohol, and various acid esters (*Annalen*, 223, 283).

6. ACID AMIDES.

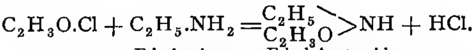
These correspond to the amines of the alcohol radicals (p. 157). The hydrogen of ammonia can be replaced by acid radicals forming primary, secondary and tertiary amides.

The following general methods for preparing primary amides are in use:—

1. The action of acid chlorides upon aqueous ammonia:—

$$C_2H_3O.Cl + 2NH_3 = \underset{\text{Acetamide.}}{C_2H_3O.NH_2} + NH_4Cl.$$

This method is especially adapted to the higher fatty acids (*Berichte*, 15, 1728). If amine bases be substituted for ammonia, mixed amides result:—



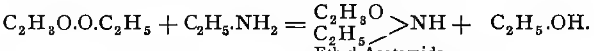
$$C_2H_3O.Cl + \underset{\text{Ethylamine.}}{C_2H_5.NH_2} = \underset{\text{Ethyl Acetamide.}}{\begin{matrix}C_2H_5\\C_2H_3O\end{matrix}>NH} + HCl.$$

The acid anhydrides have a similar action upon ammonia and the amines:—

$$\underset{\text{Acetic Anhydride.}}{(C_2H_3O)_2O} + 2\,NH_3 = \underset{\text{Acetamide.}}{C_2H_3O.NH_2} + C_2H_3O.O.NH_4.$$

2. The action of ammonia or amines upon the esters—a reaction that frequently takes place in the cold; it is best, however, to apply heat to the alcoholic solution:—

$$C_2H_3O.O.C_2H_5 + NH_3 = \underset{\text{Acetamide.}}{C_2H_3O.NH_2} + C_2H_5.OH,$$



$$C_2H_3O.O.C_2H_5 + C_2H_5.NH_2 = \underset{\text{Ethyl Acetamide.}}{\begin{matrix}C_2H_3O\\C_2H_5\end{matrix}>NH} + C_2H_5.OH.$$

This is one of the so-called reversible reactions, inasmuch as the action of alcohols upon acid amides again produces esters and ammonia (*Berichte*, 22, 24).

3. The dry distillation of the ammonium salts of the acids of this series. This procedure is adapted to the preparation of volatile amides. A mixture of the sodium salts and ammonium chloride may be substituted for the ammonium salts; the latter will be produced at first:—

$$\underset{\text{Ammonium Acetate.}}{C_2H_3O.O.NH_4} = \underset{\text{Acetamide.}}{C_2H_3O.NH_2} + H_2O.$$

A more abundant yield is obtained by merely heating the ammonium salts to about 230° (*Berichte*, 15, 979). Consult *Berichte*, 17, 848, upon the velocity and limit of the amide production.

4. The distillation of the fatty acids with potassium sulphocyanide:—

$$2C_2H_3O.OH + CN.SK = C_2H_3O.NH_2 + C_2H_3O.OK + COS.$$

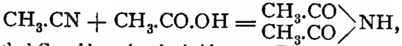
Simply heating the mixture is more practical (*Berichte*, 16, 2291, and 15, 978). In this reaction the aromatic acids yield nitriles.

5. The addition of 1 molecule of water to the nitriles of the acids (cyanides of the alcohol radicals):—

$$\underset{\text{Acetonitrile.}}{CH_3.CN} + H_2O = \underset{\text{Acetamide.}}{CH_3.CO.NH_2}.$$

This conversion is often accomplished by acting in the cold with concentrated hydrochloric acid, or by mixing the nitrile with glacial acetic acid and concentrated sulphuric acid (*Berichte*, 10, 1061). Hydrogen peroxide will also convert the nitriles, with oxygen liberation, into the amides (*Berichte*, 18, 355): $R.CN + 2H_2O_2 = R.CO.NH_2 + H_2O + O_2$.

The preceding methods are not applicable in the preparation of secondary and tertiary amides, as the acid chlorides do not generally act on the primary amides. They are obtained by heating the alkyl cyanides (the nitriles) with acids, or acid anhydrides, to 200°:—



$$CH_3.CN + CH_3.CO.OH = \begin{matrix} CH_3.CO \\ CH_3.CO \end{matrix}\!\!>NH,$$

Methyl Cyanide. Acetic Acid. Diacetamide.

$$CH_3.CN + (CH_3.CO)_2O = (CH_3.CO)_3N.$$

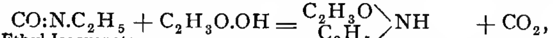
Acetic Anhydride. Triacetamide.

The secondary amides can also be prepared by heating primary amides with dry hydrogen chloride:—

$$2C_2H_3O.NH_2 + HCl = (C_2H_3O)_2NH + NH_4Cl.$$

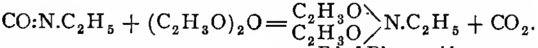
Diacetamide.

Mixed amides, which at the same time contain alcohol radicals, are further produced by the action of esters of ordinary isocyanic acid upon acids or acid anhydrides:—



$$CO{:}N.C_2H_5 + C_2H_3O.OH = \begin{matrix} C_2H_3O \\ C_2H_5 \end{matrix}\!\!>NH \quad + CO_2,$$

Ethyl Isocyanate.



$$CO{:}N.C_2H_5 + (C_2H_3O)_2O = \begin{matrix} C_2H_3O \\ C_2H_3O \end{matrix}\!\!>N.C_2H_5 + CO_2.$$

Ethyl Diacetamide.

The amides of the fatty acids are usually solid, crystalline bodies, soluble in both alcohol and ether. The lower members are also soluble in water, and can be distilled without decomposition. As they contain the basic amido-group they are able to unite directly with acids, forming salt-like derivatives (*e.g.*, $C_2H_3O.NH_2.NO_3H$), but these are not very stable, because the basic character of the amido-group is strongly neutralized by the acid radical. Furthermore, the acid radical imparts to the NH_2-group the power of exchanging a hydrogen atom with metals not very basic, forming metallic derivatives, *e.g.*, $(CH_3.CO.NH)_2.Hg$—mercury acetamide, analogous to the isocyanates (from isocyanic acid, CO:NH).

The union of the amido-group with the acid radicals (the group CO) is very feeble in comparison with its union with the alkyls in the amines (p. 158). The amides, therefore, readily decompose into their components. Heating with water effects this, although it is more easily accomplished by boiling with alkalies or acids:—

$$CH_3.CO.NH_2 + H_2O = CH_3.CO.OH + NH_3.$$

Nitrous acid decomposes the primary amides similarly (p. 161), whereby the ammonia breaks up with the evolution of nitrogen and the formation of water :—

$$C_2H_3O.NH_2 + NO_2H = C_2H_3O.OH + N_2 + H_2O.$$

Bromine in alkaline solution changes the primary amides to brom-amides (*Berichte*, 15, 407 and 752) :—

$$C_2H_3O.NH_2 + Br_2 = C_2H_3O.NHBr + HBr,$$

which then form amines (p. 160). On heating with phosphorus pentoxide, or with the chloride, they part with 1 molecule of water and become nitriles (cyanides of the alcohol radicals) :—

$$CH_3.CO.NH_2 = CH_3.CN + H_2O.$$

In this action a replacement of an oxygen atom by two chlorine atoms takes place; the resulting chlorides, like $CH_3.CCl_2.NH_2$, then lose, upon further heating, 2 molecules of ClH with the formation of nitriles :—

$$CH_3.CCl_2.NH_2 = CH_3.CN + 2HCl.$$

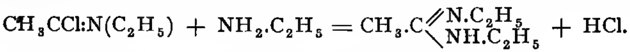
In the mixed amides, containing an alcohol radical besides the acid radical in the amido-group, PCl_5 effects a similar substitution of 2Cl for an oxygen atom. The products are the so-called *amid-chlorides*, which readily part with HCl and become *imid-chlorides* :—

$$CH_3.CCl_2.NH(C_2H_5) = CH_3.CCl:N(C_2H_5) + HCl.$$

These regenerate the amides with water :—$CH_3.CCl:N(C_2H_5) + H_2O = CH_3.CO.NH(C_2H_5) + HCl$. When heated they lose, however, hydrochloric acid and yield chlorinated bases :—

$$2CH_3.CCl:N(C_2H_5) = C_8H_{15}ClN_2 + HCl.$$

The chlorine in the imid-chlorides is very reactive; the action of ammonia on amines produces the *amidines* (see these) :—



$$CH_3CCl:N(C_2H_5) + NH_2.C_2H_5 = CH_3.C\begin{cases}N.C_2H_5\\NH.C_2H_5\end{cases} + HCl.$$

Hydrogen sulphide converts them into thio-amides.

The chlorimides, containing the group NCl, but only known in the benzene series, are isomeric with the imid-chlorides, RN:CCl. They can be converted into the latter by a molecular rearrangement (see Benzoanilide, *Berichte*, 19, 992).

Formamide, $CHO.NH_2$, the amide of formic acid, is obtained by heating ammonium formate to 230°, or ethyl formic ester with alcoholic ammonia to 100° (*Berichte*, **15**, 980); also by boiling formic acid with ammonium sulphocyanide (*Berichte* **16**, 2291). It is a liquid, readily soluble in water and alcohol, and boils with partial decomposition at 192°–195°. Heated rapidly, it breaks up into CO and NH_3; P_2O_5 liberates HCN from it.

Mercuric oxide dissolves in it with the formation of mercury formamide, $(CHO.NH)_2Hg$. This is a feebly alkaline liquid, sometimes applied as a subcutaneous injection.

Ethyl Formamide, $CHO.NH.C_2H_5$, is obtained from ethyl formic ester and ethylamine; also by distilling a mixture of the latter with chloral:—

$$CCl_3.CHO + NH_2.C_2H_5 = CHO.NH.C_2H_5 + CCl_3H.$$

It boils at 199°.

Acetamide, $C_2H_3O.NH_2$, is produced on heating a mixture of dry sodium acetate and ammonium chloride, or by digesting acetic ester with alcoholic ammonia (*Berichte*, **15**, 980). Another method consists in supersaturating glacial acetic acid with ammonia, and then distilling in a current of ammonia (*Berichte*, **18**, Ref. 436). It crystallizes in long needles, melts at 82–83°, and boils at 222° undecomposed. It dissolves with ease in water and alcohol, and when boiled with alkalies or acids, passes into acetic acid and ammonia. With acids, it forms unstable compounds, like $C_2H_5NO.NO_3H$ and $(C_2H_5NO)_2.HCl$. When the aqueous solution is boiled with mercuric oxide, the latter dissolves, and on cooling *mercury acetamide*, $(C_2H_3O.NH)_2Hg$, separates (p. 257).

Acetbromamide, $C_2H_3O.NHBr$ (p. 258), crystallizes from water and ether with 1 molecule H_2O, in large plates, and melts in an anhydrous condition at 108°.

Substituted acetamides are derived from substituted acetic esters by the action of alcoholic ammonia, and evaporation at ordinary temperatures. *Chloracetamide*, $C_2H_2ClO.NH_2$, melts at 116°, and boils at 224°-225°. *Dichloracetamide*, $C_2HCl_2O.NH_2$, melts at 96°, and boils at 233°–234°. *Trichloracetamide* melts at 136°, and boils at 238°–239°

Diacetamide, $(C_2H_3O)_2NH$, obtained by heating acetamide in a stream of HCl (p. 257), is readily soluble in water, fuses at 59°, and boils at 210°–215°.

Triacetamide, $(C_2H_3O)_3N$, is prepared by heating acetonitrile (methyl cyanide) with acetic anhydride to 200° (p. 257). It melts at 78°–79°.

Propionamide, $C_3H_5O.NH_2$, is similar to acetamide, melts at 75° and boils at 210°.

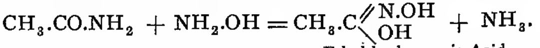
Butyramide, $C_4H_7O.NH_2$, crystallizes in leaflets, fusing at 115° and boiling at 216°. **Isobutyramide** fuses at 129°.

Isovaleramide, $C_5H_9O.NH_2$, from valeric acid, sublimes in leaflets, soluble in water and fusing at 126°.

Lauramide, $C_{12}H_{23}O.NH_2$, fuses at 102°; **Myristamide,** $C_{14}H_{27}O.NH_2$, at 104°; **Palmitamide,** $C_{15}H_{31}O.NH_2$, at 107°; **Stearamide,** $C_{18}H_{35}O.NH_2$, at 109° (*Berichte*, 15, 984 and 15, 1728). These higher amides may also be prepared by saponifying the fats with alcoholic ammonia, when the glycerol esters will react, in a manner similar to that of the monohydric alcohols.

Hydroxamic Acids.

These are produced when free hydroxylamine, or its hydrochloride, is allowed to act upon acid amides. They contain the isonitroso-group in the place of the carbonyl oxygen (*Berichte*, **22**, 2854):—



$$CH_3.CO.NH_2 + NH_2.OH = CH_3.C\left\langle\begin{matrix}N.OH\\OH\end{matrix}\right. + NH_3.$$

Ethyl-hydroxamic Acid.

They are crystalline compounds, acid in character, and form an insoluble copper salt in ammoniacal copper solutions. Ferric chloride imparts a cherry-red color to both their acid and neutral solutions.

Ethyl Hydroxamic Acid, $CH_3.C(N.OH).OH$, with $\frac{1}{2}H_2O$, is a crystalline hydrate, melting at 59°. It dissolves very easily in water and alcohol, but not in ether. Compare Benzhydroxamic acid.

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7. THIO-AMIDES.

Thio-amides of the acids, *e.g.*, thio-acetamide, $CH_3.CS.NH_2$, and thio-benzamide, $C_6H_5.CS.NH_2$, are formed by letting phosphorus sulphide act upon the acid amides (p. 250), and by the addition of H_2S to the nitriles:—

$$\underset{\text{Acetonitrile.}}{CH_3.CN} + H_2S = \underset{\text{Thio-acetamide.}}{CH_3.CS.NH_2}.$$

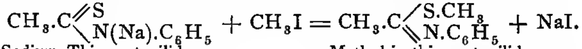
Phenyl thio-amides, in which the H of the amido-group is replaced by C_6H_5, *e.g.*, thio-acetanilide, $CH_3.CS.NH.C_6H_5$, are obtained from the anilides (see these) by the action of P_2S_5; also by acting with H_2S upon the amid-chlorides, imid-chlorides, and amidines, and by treating the latter with CS_2 (*Berichte*, **22**, 506). The thio-anilides of formic acid, *thio-formanilides*, result by the addition of H_2S to the isonitriles or isocyanides (of the benzene series):—

$$\underset{\text{Phenyl Isocyanide.}}{C_2H_5.NC} + H_2S = \underset{\text{Thioformanilide.}}{C_6H_5.NH.CHS}.$$

The thio-amides resemble the amides and are readily broken up into fatty acids, SH_2, NH_3 and amines. They manifest more of an acid character than the oxygen amides, dissolve in alkalies, and readily yield metallic derivatives by the replacement of 1 hydrogen atom of the amido-group.

In the action of hydroxylamine upon the thio-amides the S-atom is replaced by the iso-nitroso-group, with production of amidoximes (see these).

When iodides of the hydrocarbons act on the sodium compound of thio-acetanilide, iso-thio-acetanilides containing alcohol radicals result:—



$$CH_3.C\left\langle\begin{matrix}S\\N(Na).C_6H_5\end{matrix}\right. + CH_3I = CH_3.C\left\langle\begin{matrix}S.CH_3\\N.C_6H_5\end{matrix}\right. + NaI.$$

Sodium Thio-acetanilide. Methyl-isothio-acetanilide.

These are viewed as derivatives of the so-called isothio-acetamide, $CH_3.C\left\langle\begin{matrix}SH\\NH\end{matrix}\right.$. The latter compound has not yet been obtained free; it is isomeric with thio-acetamide (*Berichte*, 12, 1062, and 16, 144). The forms $CH_3.C\left\langle\begin{matrix}SH\\NH\end{matrix}\right.$ and $CH_3.C\left\langle\begin{matrix}S\\NH_2\end{matrix}\right.$ are probably tautomeric. Hydrochloric acid converts the iso-compounds having alcohol radical groups, into aniline and esters of thio-acetic acid (p. 250).

The so-called imido-thio-ethers (see these) possess a constitution like the isothio-amides.

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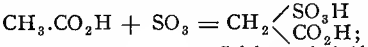
8. CYAN-, SULPHO- AND AMIDO-DERIVATIVES OF THE ACIDS.

In the acids, the hydrogen of the acid radicals can be substituted, the same as in the hydrocarbons, by the monovalent groups, SO_3H, sulpho-, CN, cyan-, NH_2, amido-, etc. The resulting derivatives, having two side groups, belong to the divalent compounds, and are in part described with the divalent alcohols and acids, for the preparation of which they serve as transition stages. Here we will merely call attention to the ordinary methods used in their production:—

The **Sulpho-derivatives** of the monobasic acids correspond perfectly to the sulpho-compounds of the alcohol radicals (p. 152), and are obtained according to similar methods:—

(1) By the action of sulphur trioxide upon the fatty acids:—

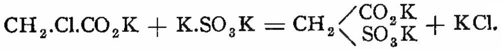


$$CH_3.CO_2H + SO_3 = CH_2\left\langle\begin{array}{l}SO_3H\\CO_2H;\end{array}\right.$$

Acetic Acid. Sulpho-acetic Acid.

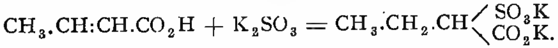
or by acting with fuming sulphuric acid on the nitriles, or amides of the acids, in which case the latter first change to acids.

(2) By heating concentrated aqueous solutions of the salts of the monosubstituted fatty acids with alkaline sulphites (p. 151):—



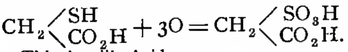
$$CH_2.Cl.CO_2K + K.SO_3K = CH_2\left\langle\begin{array}{l}CO_2K\\SO_3K\end{array}\right. + KCl.$$

Some of the sulpho-fatty acids are analogously obtained by the addition of alkaline sulphites to unsaturated acids (*Berichte*, 18, 483):—



$$CH_3.CH{:}CH.CO_2H + K_2SO_3 = CH_3.CH_2.CH\left\langle\begin{array}{l}SO_3K\\CO_2K.\end{array}\right.$$

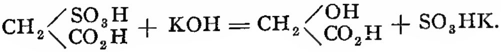
(3) By oxidizing the thio-acids corresponding to the oxy-acids with nitric acid:—



$$CH_2\left\langle\begin{array}{l}SH\\CO_2H\end{array}\right. + 3O = CH_2\left\langle\begin{array}{l}SO_3H\\CO_2H.\end{array}\right.$$

Thioglycollic Acid.

The formulas indicate these sulpho-acids to be dibasic (mixed carboxylic and sulpho-acids). They correspond to the dicarboxylic acids, like $CH_2\left\langle\begin{array}{l}CO_2H\\CO_2H\end{array}\right.$—malonic acid. They are mostly crystalline substances, easily soluble in water and deliquescent in the air. Their salts generally crystallize well. The sulpho-group in them is not so intimately combined as in the sulphonic acids of the alcohol radicals. Boiling alkalies convert them into oxy-acids:—



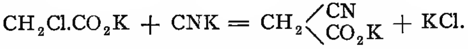
$$CH_2\left\langle\begin{array}{l}SO_3H\\CO_2H\end{array}\right. + KOH = CH_2\left\langle\begin{array}{l}OH\\CO_2H\end{array}\right. + SO_3HK.$$

Sulpho-acetic Acid, $CH_2{<}\begin{matrix}SO_2.OH\\CO_2H\end{matrix}$, is obtained by oxidizing isothionic acid, $CH_2(OH).CH_2.SO_3H$, with nitric acid. Sulphuric acid liberates it from its readily soluble barium salt. The acid crystallizes with 1½ molecules H_2O in deliquescent prisms, which fuse at 75°. The barium salt, $CH_2{<}\begin{matrix}SO_3\\CO_2\end{matrix}{>}Ba + H_2O$, forms leaflets. Pentachloride of phosphorus converts it into the chloride, $CH_2{<}\begin{matrix}SO_2Cl\\CO.Cl\end{matrix}$. By reduction of the latter with tin and hydrochloric acid thioglycollic acid, $CH_2{<}\begin{matrix}SH\\CO_2H\end{matrix}$, is produced.

Its *ethyl ester* results from the action of ethyl iodide upon its silver salt. The hydrogen atoms of the CH_2-group in this ester (as in acetoacetic and malonic esters) can be replaced by alkyls (*Berichte*, 21, 1550).

See *Berichte*, 22, 518, upon the sulpho-derivatives of the higher acids of the marsh-gas series.

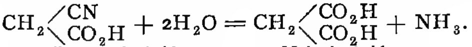
The **Cyan-derivatives** are obtained by heating the mono-halogen acids (their salts or esters) with aqueous or alcoholic potassium cyanide:—



$$CH_2Cl.CO_2K + CNK = CH_2{<}\begin{matrix}CN\\CO_2K\end{matrix} + KCl.$$

In this reaction the halogen is not only replaced by cyanogen, but very often there is a simultaneous doubling of the acid ester (*Berichte*, 21, 3166 and 3399).

As a usual thing they crystallize poorly and are unstable. When boiled with alkalies or acids they are converted into dibasic acids (p. 211):—



$$CH_2{<}\begin{matrix}CN\\CO_2H\end{matrix} + 2H_2O = CH_2{<}\begin{matrix}CO_2H\\CO_2H\end{matrix} + NH_3.$$

Cyanacetic Acid. Malonic Acid.

Cyanformic Acid, $CN.CO_2H$. In the following pages this will be considered as *cyancarbonic acid.*

Cyanacetic Acid, $CH_2(CN).CO_2H$, is derived from monochloracetic acid. It is a crystalline mass, readily soluble in water, melting at 65° (*Berichte*, 20, Ref. 477), and splitting up into CO_2 and acetonitrile, $CH_3.CN$, at 165°. Malonic acid is produced when it is boiled with alkalies or acids.

Preparation.—Boil monochloracetic ester (5 parts) with potassium cyanide (6 parts) and water (24 parts), or alcohol, until the odor of prussic acid has disappeared, then neutralize the solution with H_2SO_4, concentrate, supersaturate with sulphuric acid and withdraw the cyanacetic acid by shaking the liquid with ether.

Ethyl Cyanacetate, $CH_2{<}\begin{matrix}CN\\CO_2.C_2H_5\end{matrix}$, boils about 207°. The hydrogen of its CH_2-group is replaceable by alkyls (*Berichte*, 20, Ref. 477) and acid radicals (*Berichte*, 21, Ref. 353). Aceto-cyanacetic ester is identical with cyan-acetoacetic ester (*Berichte*, 20, Ref. 477).

α-**Cyanpropionic Acid,** $CH_3.CH(CN).CO_2H$, from *α*-brompropionic acid, yields isosuccinic acid when saponified. Its *ethyl ester* boils at 197°. The hydrogen of its CH-group can be replaced by sodium and alkyls (*Berichte*, 21, 3164). *β*-**Cyanpropionic Acid,** $CH_2(CN).CH_2.CO_2H$, from *β*-chlorpropionic acid, yields ordinary succinic acid when saponified.

CYANOGEN COMPOUNDS.

The monovalent group CN, in which trivalent nitrogen is linked with three affinities to carbon, $N{\equiv}C-$, is capable of forming quite a number of different derivatives. It shows in many respects great similarity to the halogens, chlorine, bromine, and iodine. Like these, it combines with hydrogen, forming an acid, and combines with the metals to salts which resemble and are frequently isomorphous with the haloid salts. Thus, the alkali salts assume the cube form in crystallizing, and silver cyanide is in all respects like silver chloride. Potassium and sodium burn in cyanogen gas, as in chlorine, forming cyanides. The monovalent group CN cannot exist free, but it doubles itself, just as all other monovalent groups, *e.g.*, CH_3, when it separates from its compounds, and we get the molecule:—

Dicyanogen, $C_2N_2 = NC-CN$.

In organic cyanogen compounds where CN is attached to alkyls the union of the cyanogen group is very firm. Yet the nitrogen atom in CN can be easily liberated as ammonia, and the carbon atom will pass into the carboxyl group, CO_2H. *This behavior is characteristic of cyanogen derivatives.* It may be effected by the absorption of water, which can occur by boiling with acids and alkalies:—

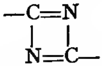
$$R-CN + 2H_2O = R-CO.OH + NH_3.$$

Nascent hydrogen causes a partial separation of nitrogen, producing amines:—

$$CH{\equiv}N + 2H_2 = CH_3-NH_2.$$

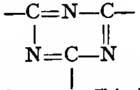
An oxygen atom can be inserted into the CH group—see cyanic acid.

A similar, partial separation accounts also for the condensation of the cyan-group to polymeric forms, *e. g.*, **dicyanogen,** C_2N_2, and **tricyanogen,** C_3N_3. The following formulas express their structure:—



Dicyanogen, Divalent.

and

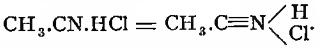


Tricyanogen, Trivalent.

Very many cyanogen derivatives readily adapt themselves to such polymerizations.

Besides the above normal cyanogen derivatives there also exist isomeric *Pseudo-* and *Iso-*cyanogen compounds. These will receive attention further on (with the cyanic acids and carbylamines).

The nitrogen atom in the cyanogen group is trivalent; it may be considered as ammonia in which carbon replaces the hydrogen atoms. This would explain why so many cyanogen derivatives, in the same manner as the amides, combine directly with the haloid acids and metallic chlorides, yielding compounds similar to the ammonium salts:—



$$CH_3.CN.HCl = CH_3.C{\equiv}N\begin{smallmatrix}\diagup H\\ \diagdown Cl\end{smallmatrix}.$$

These are, however, unstable. Perhaps it is necessary to admit (p. 258) that the halogen hydride has effected an entrance for itself in the CN group (as in $CH_3.CCl = N.CH_3$).

Yellow prussiate of potash and potassium cyanide serve as starting-out substances in the preparation of the cyanogen derivatives. Potassium cyanide is obtained by the ignition of nitrogenous organic matter with KOH or potashes (see Text-Book of Inorganic Chemistry). The direct union of carbon and nitrogen to cyanogen is only effected with difficulty. It may be accomplished by conducting nitrogen over a mixture of carbon and metallic potassium or potassium carbonate raised to a red heat. Potassium cyanide is then formed. The yield is more abundant if ammonia gas be conducted over the mixture. The ignition of carbon in ammonia gas yields ammonium cyanide:—

$$C + 2NH_3 = CN.NH_4 + H_2.$$

All these methods, however, are not applicable on a large scale.

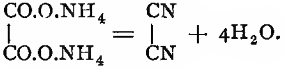
Free Cyanogen or **Dicyanogen,** $C_2N_2 = NC.CN$, is present in small quantity in the gases of the blast furnace. It is obtained by the ignition of silver or mercury cyanide:—

$$Hg(CN)_2 = C_2N_2 + Hg.$$

The transposition proceeds more readily by the addition of mercuric chloride.

It is most readily prepared from potassium cyanide. To this end the concentrated aqueous solution of 1 part KCN is gradually added to 2 parts cupric sulphate in 4 parts of water. Heat is then applied. At first a yellow precipitate of copper cyanide, $Cu(CN)_2$, is produced, but it immediately breaks up into cyanogen gas and cuprous cyanide, CuCN.

Its preparation from ammonium oxalate, through the agency of heat, is of theoretical interest:—

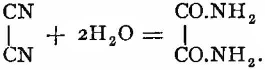


$$\begin{array}{l}CO.O.NH_4\\ |\\ CO.O.NH_4\end{array} = \begin{array}{l}CN\\ |\\ CN\end{array} + 4H_2O.$$

It is on this account to be considered as the nitrile of oxalic acid.

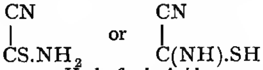
Cyanogen is a colorless, peculiar-smelling, poisonous gas, of specific gravity 26 (H = 1). It may be condensed to a mobile liquid by cold of —25°, or by a pressure of four atmospheres at ordinary temperatures. In this condition it has a sp. gr. 0.866, solidifies at —34° to a crystalline mass, and boils at —21°. It burns with a bluish-purple mantled flame. Water dissolves 4 volumes and alcohol 23 volumes of the gas.

On standing the solutions become dark and break up into ammonium oxalate and formate, hydrogen cyanide and urea, and at the same time a brown body, the so-called *azulmic acid*, $C_4H_5N_5O$, separates. With aqueous potash cyanogen yields potassium cyanide and isocyanate. In these reactions the molecule breaks down, and if a slight quantity of aldehyde be present in the aqueous solution only oxamide results:—



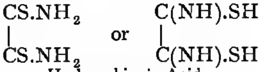
$$\begin{array}{l}CN\\ |\\ CN\end{array} + 2H_2O = \begin{array}{l}CO.NH_2\\ |\\ CO.NH_2.\end{array}$$

With hydrogen sulphide cyanogen yields *hydroflavic acid*, $C_2N_2.H_2S$ =  $\begin{array}{l}CN\\ |\\ CS.NH_2,\end{array}$ and *hydrorubianic acid*, $C_2N_2.2H_2S$ =  $\begin{array}{l}CS.NH_2\\ |\\ CS.NH_2.\end{array}$ These two compounds may be considered thioamides, or as tautomeric isothioamides (p. 260):—



$$\begin{array}{l}CN\\ |\\ CS.NH_2\end{array} \text{ or } \begin{array}{l}CN\\ |\\ C(NH).SH\end{array}$$

Hydroflavic Acid.



$$\begin{array}{l}CS.NH_2\\ |\\ CS.NH_2\end{array} \text{ or } \begin{array}{l}C(NH).SH\\ |\\ C(NH).SH\end{array}$$

Hydrorubianic Acid.

The first consists of yellow crystals, the second of red, and is best prepared by conducting cyanogen gas into an alcoholic solution of potassium sulphydrate, and adding hydrochloric acid (*Berichte*, 22, 2305). It unites with two molecules of hydroxylamine (like the thioamides) to form oxaldiamidoximes.

On heating mercuric cyanide there remains a dark substance, *paracyanogen*, a polymeric modification, $(C_2N_2)_n$. Strong ignition converts it again into cyanogen. It yields potassium cyanate with caustic potash.

Hydrocyanic Acid, CNH, Prussic Acid, is obtained from various plants containing amygdalin (from cherry-stones, bitter almonds, etc.), on standing in contact with water, when the amygdalin undergoes a fermentation, breaking up into hydrocyanic acid, sugar and oil of bitter almonds. Its production from ammonium formate by the application of heat is of theoretic interest:—

$$CHO.O.NH_4 = CHN + 2H_2O.$$

This reaction would show it to be the nitrile of formic acid.

Hydrogen cyanide may also be obtained by passing the silent electric discharge through a mixture of C_2N_2 and hydrogen:

$$C_2N_2 + H_2 = 2CNH.$$

The metallic cyanides yield it when they are distilled with mineral acids.

Anhydrous hydrocyanic acid is a mobile liquid, of specific gravity 0.697 at 18°, and becomes a crystalline solid at —15°. It boils at + 26.5°. Its odor is peculiar and resembles that of oil of bitter almonds. The acid is extremely poisonous.

The following procedure serves for the preparation of aqueous prussic acid. Finely pulverized yellow prussiate of potash (10 parts) is covered with a cooled mixture of sulphuric acid (7 parts) and water (10 to 40 parts, according to the desired strength of the prussic acid), and then distilled from a retort provided with a condenser. The heat of a sand-bath is necessary. The decomposition of the yellow prussiate occurs according to the equation:—

$$2FeCy_6K_4 + 3SO_4H_2 = Fe_2Cy_6K_2 + 3SO_4K_2 + 6CNH.$$

About half the cyanogen contained in the ferrocyanide is converted into hydrocyanic acid.

The anhydrous acid can be obtained from the hydrous by fractional distillation and dehydration by calcium chloride.

The aqueous acid decomposes readily upon standing, yielding ammonium formate and brown substances. The presence of a very slight quantity of stronger acid renders it more stable. When warmed with alkalies or mineral acids it breaks up into formic acid and ammonia:—

$$CNH + 2H_2O = CHO.OH + NH_3.$$

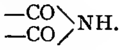
Nascent hydrogen (zinc and hydrochloric acid) reduces it to methylamine (p. 159).

Hydrocyanic acid is a feeble acid, and imparts a faint red color to blue litmus. Like the haloid acids, it reacts with metallic oxides, producing metallic cyanides. From solutions of silver nitrate it precipitates silver cyanide, a white, curdy precipitate.*

---

* In hydrocyanic acid the hydrogen, replaceable by metals, is in union with carbon, whereas, ordinarily, it is only the hydrogen of hydroxyl (in acids and alcohols) that is capable of replacements like this. The acetylenes, —C≡CH, nitro-paraffins (p. 107), aceto-acetic esters and the analogously constituted malonic esters manifest a similar deportment. In these compounds, two or three carbon valences are generally saturated by negative elements or groups, and they manifest also analogous behavior, in that their alkali salts are less stable than those with the heavy metals.

The hydrogen attached to nitrogen possesses also the function of acid hydrogen, if two affinities of the nitrogen are combined with negative groups, as in the imides:—

CO:NH and 

$$\begin{matrix}-CO\\-CO\end{matrix}\!\!>NH.$$

To detect small quantities of free prussic acid or its soluble salts, saturate the solution under examination with caustic potash, add a solution of a ferrous salt, containing some ferric salt, and boil for a short time. Add hydrochloric acid to dissolve the precipitated iron oxides. If any insoluble Prussian blue should remain, it would indicate the presence of hydrocyanic acid. The following reaction is more sensitive. A few drops of yellow ammonium sulphide are added to the prussic acid solution, and this then evaporated to dryness. Ammonium sulphocyanide will remain, and if added to a ferric salt, will color it a deep red.

Dry prussic acid combines directly with the gaseous halogen hydrides (p. 264) to form crystalline compounds like CHN.HCl, easily soluble in water and ether. The aqueous solutions rapidly decompose, yielding formic acid and ammonium salts. The acid also unites with some metallic chlorides, *e. g.*, Fe_2Cl_6, $SbCl_5$.

HALOGEN COMPOUNDS OF CYANOGEN.

These result by the action of the halogens upon metallic cyanides. The chloride and bromide can condense to tricyanides, in which we assume the presence of the tricyanogen group, C_3N_3 (p. 263).

Cyanogen Chloride, CNCl, is produced by acting with chlorine upon aqueous hydrocyanic acid. It is a mobile liquid, solidifying at —5°, and boiling at + 15.5°. It is heavier than water, and only slightly soluble in it, but readily dissolved by alcohol and ether. Its vapors have a penetrating odor, provoking tears, and acting as a powerful poison.

In preparing it, saturate a cold mercuric cyanide solution with chlorine. The cyanogen chloride which escapes on the application of heat, is conducted through a tube filled with copper turnings, to free it of chlorine. Or strongly cooled prussic acid (containing 20 per cent. CNH), is saturated with chlorine gas, the oily cyanogen chloride separated, and then distilled over mercuric oxide, to remove excess of prussic acid.

Cyanogen chloride combines with different metallic chlorides. With ammonia, it yields ammonium chloride and cyanamide, $CN.NH_2$. Alkalies decompose it into metallic cyanides and isocyanates.

Tricyanogen Chloride, $C_3N_3Cl_3$, *solid chlorcyan*, is produced when the liquid chlorine is kept in sealed tubes. It is formed directly by leading chlorine into an ethereal solution of CNH, or into anhydrous hydrocyanic acid exposed to direct sunlight (*Berichte*, **19**, 2056). It appears, too, in the distillation of cyanuric acid, $C_3O_3N_3H_3$, with phosphorus pentachloride. It crystallizes in shining needles or leaflets, melts at 146°, and boils at 190°. It is not very soluble in cold water, but readily in alcohol and ether. Its vapor density equals 92 ($H = 1$). When boiled with acids or alkalies, it breaks up into hydrochloric and cyanuric acids (*Berichte*, **19**, Ref. 599):—

$$C_3N_3Cl_3 + 3H_2O = C_3N_3(OH)_3 + 3HCl.$$

Cyanogen Bromide, CNBr, is obtained when bromine acts on anhydrous prussic acid or upon mercuric cyanide :—

$$Hg(CN)_2 + 2Br_2 = HgBr_2 + 2CNBr.$$

It is a very volatile, crystalline substance, readily soluble in water, alcohol and ether. On heating the anhydrous bromide or its ethereal solution in sealed tubes to 130–140°, it becomes polymeric **tricyanogen bromide**, $C_3N_3Br_3$. The latter is more easily obtained by heating dry yellow or red prussiate of potash with bromine at 250° (*Berichte*, 16, 2893), or on conducting HBr into the ethereal solution of CNBr (*Berichte*, 18, 3262). It is an amorphous white powder, soluble in ether and benzene. It melts about 300°, and is volatile at higher temperatures. It decomposes in moist air, or upon boiling with water, into HBr and cyanuric acid.

Cyanogen Iodide, CNI, is prepared by subliming a mixture of mercuric cyanide (1 molecule) and iodine (2 molecules); or by adding iodine to a concentrated aqueous solution of potassium cyanide. The cyanogen iodide which results is withdrawn by ether. It has a sharp odor, dissolves in water, alcohol and ether, and sublimes near 45°, without melting, in brilliant white needles. Ammonia converts it into cyanamide and ammonium iodide.

Cyanuric Iodide, $C_3N_3I_3$, is produced by the action of hydriodic acid upon cyanuric chloride. It is a dark brown, insoluble powder. At 125° water decomposes it into hydrogen iodide and cyanuric acid. At 200° it readily breaks up into iodine and paracyanogen, $(CN)_n$ (*Berichte*, 19, Ref. 599).

METALLIC DERIVATIVES OF CYANOGEN.

The metallic derivatives of cyanogen have already been considered in inorganic chemistry. Here attention will only be directed to certain generalizations.

The properties of and the methods of preparing the metallic cyanides vary greatly. The alkali cyanides may be formed by the direct action of these metals upon cyanogen gas; thus, potassium burns with a red flame in cyanogen, at the same time yielding potassium cyanide, $C_2N_2 + K_2 = 2CNK$. The strongly basic metals dissolve in hydrocyanic acid, separating hydrogen and forming cyanides. A more common procedure is to act with the acid upon metallic oxides and hydroxides: $2CNH + HgO = Hg(CN)_2 + H_2O$. The insoluble cyanides of the heavy metals are obtained by the double decomposition of the metallic salts with potassium cyanide.

The cyanides of the light metals, especially the alkali and alkaline earths, are easily soluble in water, react alkaline and are decomposed by acids, even carbon dioxide, with elimination of hydrogen cyanide; yet they are very stable, even at a red heat, and sustain no change. The cyanides of the heavy metals, however, are mostly insoluble, and are only decomposed, or not at all, by the strong acids. When ignited the cyanides of the noble metals suffer decomposition, breaking up into cyanogen gas and metals.

The following simple cyanides may be mentioned :—

Potassium Cyanide, KCN, crystallizes in cubes or octahedra, and fuses at a bright red heat to a clear liquid. In moist air it deliquesces and gives up (by the action of carbon dioxide) hydrogen cyanide. It is scarcely soluble in absolute alcohol, but dissolves readily in aqueous alcohol. The best mode of preparing chemically pure potassium cyanide consists in conducting prussic acid into an alcoholic solution of KOH (in 90 per cent. alcohol). Take 1 part KOH for 3 parts of the yellow prussiate (p. 266). The potassium cyanide separates as a powder or jelly, which is drained upon a filter. The so-called Liebig potassium cyanide, occurring in trade, contains potassium cyanide and isocyanate. It is made by igniting a mixture of dry yellow prussiate of potash (8 parts) with pure potashes (3 parts):—

$$FeCy_6K_4 + CO_3K_2 = 5KCy + CNOK + CO_2 + Fe.$$

At present chemically pure potassium cyanide is obtained by mere ignition of potassium ferrocyanide:—

$$Fe(CN)_6K_4 = 4KCN + FeC_2 + N_2.$$

The exceedingly finely divided iron carbide which adheres to the salt is removed by filtering the molten mass through porous clay crucibles.

The aqueous or alcoholic solution becomes brown on exposure, and when boiled, rapidly decomposes into potassium formate and ammonia. If fused in the air or with metallic oxides which are readily reduced, potassium cyanide absorbs oxygen, and is converted into potassium isocyanate. When fused with sulphur it yields potassium thiocyanate.

Ammonium Cyanide, NH_4CN, is formed by the direct union of CNH with ammonia, by heating carbon in ammonia gas, and by conducting carbon monoxide and ammonia through red-hot tubes. It is best prepared by subliming a mixture of potassium cyanide or dry ferrocyanide with ammonium chloride. An aqueous solution of it may be made by distilling the solution of ferrocyanide and ammonium chloride. It yields colorless cubes, easily soluble in alcohol and subliming at 40°, with partial decomposition into NH_3 and CNH. When preserved it becomes dark in color and decomposes.

Mercuric Cyanide, $Hg(CN)_2$, is obtained by dissolving mercuric oxide in hydrocyanic acid, or by boiling Prussian blue (8 parts) and mercuric oxide (1 part) with water, until the blue coloration disappears. It dissolves readily in hot water (in 8 parts cold water), and crystallizes in bright, shining, quadratic prisms. When heated it yields cyanogen and mercury (p. 264).

Silver Cyanide, AgCN, is precipitated as a white, curdy compound from silver solutions by potassium cyanide or prussic acid. It resembles silver chloride very much. It darkens on exposure to the air, and dissolves readily in ammonium hydrate and potassium cyanide.

From some reactions, it would seem that silver cyanide may contain the isocyanogen group, $C \equiv N$ —, and that silver, consequently, is linked to nitrogen (as in silver nitrite, NO_2Ag, p. 106). Compare Carbylamines (p. 287).

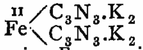
Compound Metallic Cyanides. The cyanides of the heavy metals insoluble in water dissolve in aqueous potassium cyanide, forming crystallizable double cyanides, which are soluble in water. Most of these compounds behave like double salts. Acids decompose them in the cold, with disengagement of hydrocyanic acid and the precipitation of the insoluble cyanides:—

$$AgCN.KCN + HCl = AgCN + KCl + CNH.$$

In others, however, the metal is in more intimate union with the cyanogen group, and the metals in these cannot be detected by the usual reagents. Iron, cobalt, platinum, also chromium and manganese in their *ic* state, form cyanogen derivatives of this class. The stronger acids do not eliminate prussic acid from them, even in the cold, but hydrogen acids are set free, and these are capable of producing salts:—

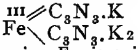
$$\underset{\text{Potassium Ferrocyanide.}}{Fe(CN)_6K_4} + 4HCl = \underset{\text{Hydroferrocyanic Acid.}}{Fe(CN)_6H_4} + 4KCl.$$

It may be assumed that polymeric cyanogen groups—dicyanogen and tricyanogen (p. 263)—are present in these derivatives of cyanogen:—



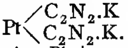
$$\overset{II}{Fe}\left\langle\begin{matrix}C_3N_3.K_2\\C_3N_3.K_2\end{matrix}\right.$$

Potassium Ferrocyanide.



$$\overset{III}{Fe}\begin{matrix}\diagup\!\!\diagup C_3N_3.K\\\diagdown C_3N_3.K_2\end{matrix}$$

Potassium Ferricyanide.



$$Pt\left\langle\begin{matrix}C_2N_2.K\\C_2N_2.K.\end{matrix}\right.$$

Potassium Platinocyanide.

This view is sustained by the fact that these cyanides, although soluble in water, are yet not poisonous. We do not know of a sharp line of difference between cyanides of the first and those of the second variety; different compounds, *e. g.*, potassium gold cyanide, $\overset{III}{Au}(CN)_4K$, show an intermediate behavior. The most important compound cyanides have been already treated in the Inorganic Chemistry.

Nitroprussides. These arise on treating the ferrocyanides with nitric acid. The most important of them is

Sodium Nitroprusside. Its constitution has not yet been definitely determined (*Berichte*, 15, 2613). The simplest expression of it is given by the formula, $Fe(CN)_5(NO)Na_2 + 2H_2O$. It crystallizes in beautiful red rhombic prisms, readily soluble in water. Sunlight decomposes it into nitric oxide and Prussian blue.

Preparation.—Heat pulverized potassium ferrocyanide with two parts concentrated nitric acid, diluted with an equal volume of water, until ferric chloride ceases to produce a blue precipitate. The cooled solution is filtered off from the separated saltpetre, saturated with soda, and evaporated until near the point of crystallization, when 3–4 parts of alcohol are added.

Sodium nitroprusside serves as a very delicate reagent for alkaline sulphides, which give with it an intense violet coloration even in very dilute solution.

It yields precipitates with most of the heavy metals. When hydrochloric acid is added to the nitroprussides, *hydrogen nitroprusside,* $Fe(CN)_5(NO)H_2 + H_2O$, is liberated. This crystallizes in vacuo from its aqueous solution, in dark-red prisms.

OXYGEN COMPOUNDS OF CYANOGEN.

The empirical formula, CNOH, of cyanic acid, has two possible structures:—

$$\underset{\text{Normal Cyanic Acid.}}{N\equiv CO-H} \quad \text{and} \quad \underset{\text{Isocyanic Acid.}}{CO=N-H.}$$

These formulas are probably tautomeric, so that they can both be assigned to the known cyanic acid. The difference between them is first observed when hydrogen is replaced by radicals. The ordinary salts of cyanic acid appear to be derivatives of the *isocyanic acid*, CO:NH (or carbimide, the imide of carbonic acid), as isocyanic esters are produced by the action of alkyl iodides upon the silver salt. The ordinary cyanic esters are constituted according to the formula, CO:NR, and are termed isocyanic esters, while the esters of normal cyanic acid, CN.OR, are designated cyanetholines (p. 273).

Ordinary **Cyanic Acid**, CONH, is obtained by heating polymeric cyanuric acid. The vapors which distil over are condensed in a strongly cooled receiver.

The acid is only stable below 0°, and is a mobile, very volatile liquid, which reacts strongly acid, and smells very much like glacial acetic acid. It produces blisters upon the skin. About 0°, the aqueous solution is rapidly converted into carbon dioxide and ammonia:—

$$CONH + H_2O = CO_2 + NH_3.$$

At 0°, the aqueous cyanic acid passes rapidly into the polymeric *cyamelide*—a white, porcelain-like mass, which is insoluble in water, and when distilled reverts to cyanic acid. Above 0°, the conversion of liquid cyanic acid into cyamelide occurs, accompanied by explosive foaming. Cyanic acid dissolves in alcohols, yielding esters of allophanic acid.

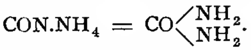
The salts of the above acid are obtained by double decomposition from the potassium salt; those of the heavy metals are insoluble in water, and those of the earths are precipitated by alcohol. Heat decomposes both varieties into CO_2 and salts of cyanamide (see this).

Potassium Isocyanate, CO:NK, *ordinary cyanate of potassium*, is formed in the oxidation of potassium cyanide in the air or with readily reducible metallic oxides (CNK + O = CO:NK). It results, too, on conducting dicyanogen, or cyanogen chloride into caustic potash (*Berichte*, 13, 2201). The salt crystallizes in shining leaflets, resembling potassium chlorate, and dissolves readily in cold water, but with more difficulty in hot alcohol. In aqueous solution it decomposes rapidly into ammonia and potassium carbonate.

Preparation.—Fuse in a crucible a mixture of dehydrated yellow prussiate of potash (8 parts), potashes (3 parts), and gradually add, while stirring, lead oxide or minium (15 parts): $CNK + PbO = CNOK + Pb$. The reduced lead melts together on the bottom of the vessel. The white mass is poured out and the potassium cyanate extracted with alcohol.

Potassium isocyanate precipitates aqueous solutions of the heavy metals. The lead, silver and mercurous salts are white, the cupric salt is green in color.

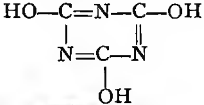
Ammonium cyanate, $CN.O.NH_4$ or $CO:N(NH_4)$, is a white crystalline powder, formed by contact of cyanic acid vapors with dry ammonia. Caustic potash decomposes it into potassium isocyanate and ammonia. On evaporating the aqueous solution it passes into isomeric urea:—



$$CON.NH_4 = CO\begin{cases}NH_2\\NH_2\end{cases}.$$

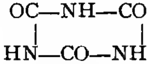
The cyanates of the primary and secondary amines are similarly converted into alkylic ureas, whereas the salts of the tertiary amines remain unchanged.

Three molecules of CNOH condense to *Tricyanic* or *Cyanuric Acid*, $C_3N_3O_3H_3$ (p. 263). Here again two structural cases are possible:—



Normal Cyanuric Acid.

and



Isocyanuric Acid or Tricarbimide.

Ordinary cyanuric acid is most probably constituted according to formula (1), because when sodium alcoholates act upon cyanuric bromide, $C_3N_3Br_3$, and alkyl iodides upon ordinary silver cyanate esters of normal cyanuric acid result (p. 275). Isocyanuric acid (formula 2) is not known in a free state, and is probably tautomeric with normal cyanuric acid, since upon saponifying the isocyanuric esters (p. 276), constituted according to the carbimide formula (2), ordinary cyanuric acid invariably results (*Berichte*, 20, 1056).

Ordinary Cyanuric Acid, $C_3O_3N_3H_3$, probably normal cyanuric acid, $C_3N_3(OH)_3$ (see above), is obtained from tricyanogen chloride, $C_3N_3Cl_3$, by boiling the latter with water and alkalies (see above).

Dilute acetic acid added to a solution of potassium isocyanate, gradually separates primary potassium isocyanate, $C_3N_3O_3H_2K$, from which mineral acids release cyanuric acid. It appears, too, on heating urea:—

$$3CON_2H_4 = C_3O_3N_3H_3 + 3NH_3.$$

Preparation.—Carefully heat urea until the disengagement of ammonia ceases and the mass, which at first fused, has become solid again. The residue is dissolved in potash and the cyanuric acid precipitated with hydrochloric acid. A better plan is to lead dry chlorine gas over fused urea at a temperature of 130–140° :—

$$3CON_2H_4 + 3Cl = C_3O_3N_3H_3 + 2NH_4Cl + HCl + N.$$

Cold water is employed to remove the ammonium chloride from the residue, and the latter recrystallized from hot water.

Cyanuric acid is more easily obtained by heating tribromcyanide with water (*Berichte*, 16, 2893).

Cyanuric acid crystallizes from aqueous solution with 2 molecules of water ($C_3N_3O_3H_3 + 2H_2O$) in large rhombic prisms. It is soluble in 40 parts cold water, and easily soluble in hot water and alcohol. When boiled with acids it decomposes into carbonic acid and ammonia. When distilled it breaks up into cyanic acid. PCl_5 converts it into tricyanogen chloride.

Cyanuric acid is tribasic and yields three series of salts, all of which crystallize well. The salts of the heavy metals are not soluble in water. A characteristic salt is the trisodium salt, $C_3N_8O_3Na_3$. This separates from aqueous solutions of cyanuric acid upon warming them with concentrated sodium hydroxide. It forms minute needles.

Two supposed isomeric cyanuric acids are identical with ordinary cyanuric acid (*Berichte*, 19, 2022).

1. ESTERS OF THE CYANIC ACIDS.

Those of normal cyanic acid, CN.OH (p. 271), result when cyanogen chloride acts upon sodium alcoholates :—

$$CNCl + C_2H_5\,ONa = CN.O.C_2H_5 + NaCl.$$

They are also termed *cyanetholines*. They are liquids, of ethereal odor, are insoluble in water, and suffer decomposition when distilled. The ethyl ester is the only one that has been closely studied.

Ethyl Cyanic Ester, $CN.O.C_2H_5$, *cyanetholine*, is obtained by the action of cyanogen chloride or iodide upon a solution of sodium ethylate in absolute alcohol. On diluting with water it precipitates out in the form of a colorless oil, of sp. gr. 1.127 at 15°. It dissolves readily in alcohol and ether. When boiled with caustic potash it decomposes into CO_2, NH_3 and ethyl alcohol. Acid esters of isocyanuric acid are produced when it is boiled with hydrochloric acid. It polymerizes into solid ethyl cyanuric esters after standing some time.

The homologous esters are prepared in a similar manner, but they have been but little investigated.

Esters of Isocyanic Acid, CO:NH, ordinary cyanic acid esters. *Würtz* prepared these, in 1848, by distilling potassium ethyl sulphate with potassium isocyanate :—

$$SO_4K(C_2H_5) + CO{:}NK = CO{:}N.C_2H_5 + SO_4K_2.$$

Esters of isocyanuric acid are formed at the same time, in consequence of polymerization. Isocyanic esters are produced, too, by oxidizing the carbylamines with mercuric oxide :—

$$C_2H_5.NC + O = C_2H_5.N{:}CO;$$

and by the action of silver isocyanate upon alkyl iodides :—

$$C_2H_5I + CO{:}NAg = CO{:}N.C_2H_5 + AgI.$$

These esters are volatile liquids, boiling without decomposition, and possessing a very disagreeable, penetrating odor, which provokes tears. They are decomposed by water and alcohol, but dissolve without decomposition in ether. On standing they pass rather rapidly into the polymeric isocyanuric esters.

In all their reactions they behave like carbimide derivatives. Heated with KOH they become primary amines and potassium carbonate (p. 159) :—

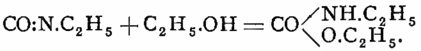
$$CO{:}N.C_2H_5 + 2KOH = CO_3K_2 + NH_2.C_2H_5.$$

Acids in aqueous solution behave similarly :—

$$CO{:}N.C_2H_5 + H_2O + HCl = CO_2 + C_2H_5.NH_2.HCl.$$

With the amines and ammonia they yield alkylic ureas (see these). Water breaks them up at once into CO_2 and dialkylic ureas. In this decomposition amines form first, CO_2 being set free, and these combine with the excess of isocyanic ester to dialkylic ureas (see these).

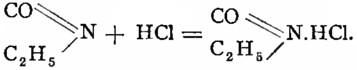
The esters of isocyanic acid unite with alcohol, yielding esters of carbaminic acid :—



$$CO{:}N.C_2H_5 + C_2H_5.OH = CO\Big\langle\begin{matrix}NH.C_2H_5\\ O.C_2H_5.\end{matrix}$$

They react similarly with the polyvalent alcohols, forming complex carbaminic acid esters (*Berichte*, 18, 968).

As derivatives of ammonia the isocyanic esters are capable of combining directly with the haloid acids :—



$$\begin{matrix}CO\\ C_2H_5\end{matrix}\Big\rangle N + HCl = \begin{matrix}CO\\ C_2H_5\end{matrix}\Big\rangle N.HCl.$$

Water decomposes these products at once into CO_2 and amine salts. They very probably are identical with the alkyl urea chlorides, $CO\Big\langle\begin{matrix}NH.C_2H_5\\ Cl\end{matrix}$ (see these), from which the isocyanic esters are again separated by distillation with lime.

Methyl Isocyanic Ester, $CO:N.CH_3$, methyl carbimide, is obtained by distilling potassium methyl sulphate with potassium isocyanate. It is a very volatile liquid, boiling at 44°. When boiled with KOH it forms methylamine, $CH_3.NH_2$.

Ethyl Isocyanic Ester, $CO:N.C_2H_5$, ethyl carbimide. This boils at 60°, and has the specific gravity of 0.891. It produces ethylamine with boiling alkalies; with sodium ethylate it yields triethylamine:—

$$CO:N.C_2H_5 + 2C_2H_5.ONa = CO_3Na_2 + N(C_2H_5)_3.$$

Isoamyl Isocyanic Ester, $CO:N.C_5H_{11}$, amyl carbimide, from amyl alcohol of fermentation, boils near 100°.

Allyl Isocyanic Ester, $CO:N.C_3H_5$, is obtained by heating allyl iodide and potassium cyanate. It boils at 82°.

2. ESTERS OF THE CYANURIC ACIDS.

The esters of the normal cyanuric acid, $C_3N_3(OH)_3$ (p. 272), are formed, as already observed, by the polymerization of the cyanic esters (cyanetholines) after long standing:—

$$3CN.O.C_2H_5 = C_3N_3(O.C_2H_5)_3,$$

and are produced directly, together with the cyanic esters, in the preparation of the latter, by conducting cyanogen chloride into sodium alcoholates.

A simpler procedure is to act upon the sodium alcoholates with cyanuric chloride or bromide (*Berichte*, 18, 3263 and 19,2063):—

$$C_3N_3Cl_3 + 3Na.O.C_2H_5 = C_3N_3(O.C_2H_5)_3 + 3NaCl.$$

The normal cyanuric esters are also formed by the action of alkyl iodides upon silver cyanurate, $C_3N_3(OAg)_3$ at 100°. Since, however, the normal esters, under the influence of heat, are transposed into the isomeric isocyanuric esters (see below), the latter are produced in large quantities even at low temperatures, while at elevated temperatures they are the only products (*Berichte*, 18, 3269). The separation of the isomeric esters may be effected by the aid of mercuric chloride, since only the normal cyanuric derivatives yield with the latter double compounds, which are characteristic (see, on contrary, Hofmann, *Berichte*, 19, 2093).

The normal cyanuric esters, on digesting with the alkalies, break up into cyanuric acid and alcohol. They combine with six atoms of bromine. PCl_5 converts them into cyanuric chloride.

Methyl Cyanuric Ester, $C_3N_3(O.CH_3)_3$, crystallizes from hot water or alcohol in needles, melting at 135°. It boils, with scarcely any alteration, at 160°–170°. The distillate contains but traces of the iso-ether. If it be boiled for some time in connection with a return cooler, the conversion into isomeric isocyanuric ester is complete. It dissolves in concentrated HCl, and is reprecipitated unchanged by ammonia. Methyl chloride and cyanuric acid are produced on boiling with hydrochloric acid.

Ethyl Cyanuric Ester, $C_3N_3(O.C_2H_5)_3$, is produced when sodium alcoholate acts upon cyanogen bromide, or cyanuric chloride (see above); also from methyl cyanuric ester, and normal methyl thio-cyanuric ester, when boiled with sodium ethylate and alcohol. It crystallizes in needles, melts at 29°, and boils unaltered at 275°. Prolonged boiling, in connection with a return cooler, gradually leads to the isocyanuric ester (melting at 95°).

Partial saponification of the normal cyanuric esters by NaOH or $Ba(OH)_2$ gives rise to normal dialkyl cyanuric acids; these, when heated, rearrange themselves into dialkyl isocyanuric acids (*Berichte*, 19, 2067).

Dimethyl Cyanuric Acid, $C_3N_3(O.CH_3)_2.OH$, crystallizes in small leaflets, melting at 160°–180°, and suddenly passes into dimethyl isocyanuric acid (melting at 222°). This change is accompanied by the evolution of much heat.

Diethyl Cyanuric Acid, $C_3N_3(O.C_2H_5)_2OH$, also melts at 160°–180°, and is suddenly converted into diethyl isocyanuric acid (m. p. 173°) (*Berichte*, 18, 3268).

When acid chlorides act upon silver cyanurate mixed anhydrides are formed, and these are again resolved into their components upon heating with water (*Berichte*, 18, 3261 and 19, 311).

Cyanuric Triacetate, $C_3N_3(O.C_2H_3O)_3$, melts with partial decomposition at 170°.

Esters of Isocyanuric Acid, $C_3O_3(N.CH_3)_3$, Tricarbimide esters, are formed together with the isocyanic esters, when the latter are prepared by the distillation of KCNO with potassium ethyl or methyl sulphate. We have already spoken of their formation as a result of the molecular transposition of the cyanuric esters. They are solid crystalline bodies, soluble in water, alcohol, and ether, and may be distilled without decomposition. They pass into primary amines and potassium carbonate when boiled with alkalies, similar to the isocyanates:—

$$C_3O_3(N.C_2H_5)_3 + 6KOH = 3CO_3K_2 + 3NH_2.C_2H_5.$$

Methyl Isocyanuric Ester, $C_3O_3(N.CH_3)_3$, crystallizes in bright prisms. It melts at 175°, and boils undecomposed at 296°. Heated with PCl_5, chlormethyl isocyanuric ester, $C_3O_3(N.CH_2Cl)_3$, is produced, whereas cyanuric chloride results from normal methyl cyanuric ester (*Berichte*, 19, 2087).

Ethyl Isocyanuric Ester, $C_3O_3(N.C_2H_5)_3$, consists of large rhombic prisms, melting at 95° and boiling at 276°. It volatilizes with steam.

Dialkyl Isocyanuric Esters, or **Isocyanuric Dialkyl Esters**, as $C_3O_3(N.CH_3)_2NH$, are formed, together with the trialkyl esters and in the distillation of monoalkyl ureas. They are also obtained from the normal dialkyl cyanuric acids by a rearrangement in consequence of the action of heat (*Berichte*, 19, 2069, 2077). They volatilize without decomposition, and, when boiled with alkalies, break up into carbonate, primary amine and ammonia. See *Berichte*, 19, 2094, upon the structure of the dialkyl isocyanuric acids.

Dimethyl-isocyanuric Acid, $C_3O_3(N.CH_3)_2.NH$, crystallizes from water in needles, or leaflets, melting at 222°. Its silver salt crystallizes with ½ molecule of water, $C_3O_3(NCH_3)_2.NAg + \frac{1}{2}H_2O$.

Diethyl-cyanuric Acid, $C_3O_3(N.C_2H_5)_2.NH$, crystallizes in hexagonal prisms, melting at 173°, and distilling without decomposition.

SULPHUR COMPOUNDS OF CYANOGEN.

The thiocyanic acids are :—

$N\equiv C-SH$	and	$S=C=NH$.
Thiocyanic Acid. Sulphocyanic Acid.		Isothiocyanic Acid. Thiocarbimide.

These correspond to the two isomeric cyanic acids (p. 271).

The known thiocyanic acid and its salts (having the group NC.S—) are constituted according to the first formula. They are obtained from the cyanides by the addition of sulphur, just as the isocyanates result by the absorption of oxygen. The different union of sulphur and oxygen in this instance is noteworthy :—

$$CNK + O = CO{:}NK. \qquad CNK + S = CN.SK.$$

Isothiocarbimide, CS:NH, and its salts are not known. Its esters (the mustard oils) do, however, exist and are isomeric with those of sulphocyanic acid.

Thiocyanic Acid, CN.SH, sulphocyanic acid, is obtained by distilling its potassium salt with dilute sulphuric acid, or decomposing the mercury salt with dry H_2S or HCl. It is a liquid, with a penetrating odor, and solidifies at —12.5°. It is soluble in water and alcohol. Its solutions react acid. The free acid, and also its salts, color solutions of ferric salts a dark red. The free acid decomposes readily, especially in the presence of strong acids, into hydrogen cyanide and perthiocyanic acid, $C_2N_2S_3H_2$.

The alkali thiocyanates, like the isocyanates, are obtained by fusing the cyanides with sulphur.

Potassium Thiocyanate, CN.SK, sulphocyanate of potash, crystallizes from alcohol in long, colorless prisms, which deliquesce in the air.

Preparation.—Fuse 32 parts sulphur with 17 parts dry potassium carbonate, add 46 parts dehydrated yellow prussiate of potash, and again heat until the latter is completely decomposed. The fusion is finally exhausted with alcohol.

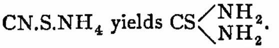
The *sodium salt* is very deliquescent, and occurs in the saliva and urine of different animals.

Ammonium Thiocyanate, $CN.S.NH_4$, is formed on heating prussic acid with yellow ammonium sulphide, or a solution of ammonium cyanide with sulphur. It is most readily obtained by heating CS_2 with alcoholic ammonia :—

$$CS_2 + 4NH_3 = CN.S.NH_4 + (NH_4)_2S.$$

A mixture of 300 parts concentrated ammonia solution, 300 parts strong alcohol, and 70–80 parts carbon disulphide, is permitted to stand for a day. Two-thirds of the liquid are then distilled off (the distillate, consisting of alcohol and some ammonium thiocyanate, may be used in a second preparation), and the residue carefully evaporated until crystallization sets in.

The salt crystallizes in large, clear prisms, which readily dissolve in water and alcohol. It melts at 147°, and at 170° molecular transposition into thiourea occurs (similar to ammonium cyanate (p. 272):—



$$CN.S.NH_4 \text{ yields } CS\begin{cases} NH_2 \\ NH_2 \end{cases}.$$

The salts of the heavy metals are mostly insoluble, and are obtained by precipitation. The *mercury salt*, $(CN.S)_2Hg$, is a gray, amorphous precipitate, which burns on ignition and swells up strongly (Pharaoh's serpents). The *ferric salt*, $(CN.S)_6Fe_2$, is a black, deliquescent mass, dissolving in water with a deep red color.

Cyanogen Sulphide, $(CN)_2S$, is formed when cyanogen iodide in ethereal solution, acts on silver thiocyanate:—

$$CN.S.Ag + CNI = AgI + (CN)_2S.$$

The product is extracted with carbon disulphide, and the solution evaporated. Cyanogen sulphide forms rhombic plates, melting at 65° and subliming at 30°. Its odor resembles that of the iodide, and the compound dissolves in water, alcohol and ether. KOH breaks it up into potassium thiocyanate and isocyanate:—

$$(CN)_2S + 2KOH = CN.SK + CO.NK + H_2O.$$

Pseudo-Cyanogen Sulphide, $C_3N_3HS_2$, is formed in the oxidation of potassium sulphocyanide with nitric acid or chlorine. It is a yellow, amorphous powder insoluble in water, alcohol and ether. It dissolves with a yellow color in alkalies.

Kanarine is similar to and probably identical with pseudo-cyanogen sulphide. It is obtained from KCNS by electrolysis, or by oxidation with $KClO_3$ and HCl (*Berichte*, 17, Ref. 279, and 18, Ref. 676). It is applied as a yellow or orange dye for wool and does not require a mordant.

ESTERS OF THE THIOCYANIC ACIDS.

Those of normal thiocyanic acid, CN.SH, are obtained by distilling organic salts of sulphuric acid in concentrated aqueous solution with potassium sulphocyanide, or by heating with alkyl iodides:—

$$CN.SK + C_2H_5I = CN.S.C_2H_5 + KI.$$

Further, by the action of CNCl upon salts of the mercaptans:—

$$C_2H_5.SK + CNCl = C_2H_5.S.CN + KCl.$$

They are liquids, not soluble in water, and possess a leek-like odor. Nascent hydrogen (zinc and sulphuric acid) converts them into hydrocyanic acid and mercaptans:—

$$CN.S.C_2H_5 + H_2 = CNH + C_2H_5.SH.$$

With aqueous potash they behave as follows:—

$$2CN.S.C_2H_5 + 2KOH = (C_2H_5)_2S_2 + CNK + CONK + H_2O.$$

On digesting with alcoholic potash the reaction is:—

$$CN.S.C_2H_5 + KOH = CN.SK + C_2H_5.OH.$$

The isomeric mustard oils do not afford any potassium sulphocyanate. With H_2S they yield the dithiourethanes, whereas the isomeric mustard oils are not attacked, or decompose into CS_2 and amines. Boiling nitric acid oxidizes them to alkylsulphonic acids with separation of the cyanogen group.

Methyl Thiocyanic Ester, $CN.S.CH_3$, boils at 133°, and has a specific gravity 1.088 at 0°. When heated to 180–185° it is converted into the isomeric methyl-isothiocyanic ester, with simultaneous polymerization to trithiocyanic ester, $C_3N_3S_3(CH_3)_3$ (*Berichte*, 18, 2197).

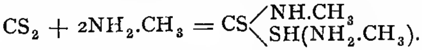
Ethyl Thiocyanic Ester, $CN.S.C_2H_5$, boils at 142°. Its specific gravity equals 1.033 at 0°. It combines directly with the haloid acids.

Isopropyl Thiocyanic Ester, $CN.S.C_3H_7$, boils at 152–153°. The **isoamyl ester,** $CN.S.C_5H_{11}$, boils at 197°.

Allyl Thiocyanic Ester, $CN.S.C_3H_5$, is formed when allyl iodide or bromide acts upon alcoholic potassium thiocyanate at 0°. When heat is applied allyl mustard oil, $CS:N.C_3H_5$, results by molecular transposition. It is produced, too, when CNCl acts upon lead allyl mercaptide. A yellow, oily liquid, smelling somewhat like CNH, and boiling at 161°. Its specific gravity equals 1.071 at 0°. On boiling it rapidly changes to isomeric allyl mustard oil, $CS:N.C_3H_5$; at ordinary temperatures the conversion is gradual. In the cold zinc and hydrochloric acid decompose the ester into CNH and allyl mercaptan, $C_3H_5.SH$.

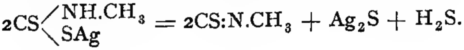
The esters of isothiocyanic acid, CS:NH, are termed mustard oils, from their most important representative. They may also be considered as thiocarbimide derivatives. They are formed:—

1. By mixing carbon disulphide with primary (or secondary) amines in alcoholic, or better, ethereal solution. By evaporation we get amine salts of alkyl carbaminic acids (see these):—



$$CS_2 + 2NH_2.CH_3 = CS\left\langle\begin{array}{l}NH.CH_3\\SH(NH_2.CH_3).\end{array}\right.$$

On adding silver nitrate, mercuric chloride or ferric chloride, to the aqueous solution of these salts, formed with primary amines, and then heating to boiling, the metallic compounds first precipitated decompose into metallic sulphides, hydrogen sulphide and mustard oils, which distil over with steam:—

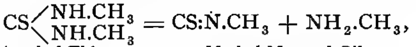


$$2CS\left\langle\begin{array}{l}NH.CH_3\\SAg\end{array}\right. = 2CS:N.CH_3 + Ag_2S + H_2S.$$

Hofmann's mustard oil test for the detection of primary amines (p. 162) is based on this behavior.

It is advisable to use ferric chloride (*Berichte*, 8, 108), because mercuric chloride will desulphurize the mustard oils, and the latter will be transposed into dialkyl ureas. Iodine, too, forms mustard oils from the amine salts of the dithiocarbaminic acids, but the yield is small.

2. By distilling the dialkylic thio-ureas (see these) with phosphorus pentoxide (*Berichte*, 15, 985):—



$$CS\begin{matrix} \diagup NH.CH_3 \\ \diagdown NH.CH_3 \end{matrix} = CS{:}N.CH_3 + NH_2.CH_3,$$

Dimethyl Thio-urea. Methyl Mustard Oil.

and by heating the isocyanic esters with P_2S_5 (*Berichte*, 18, Ref. 72): $CO{:}N.C_2H_5$ yields $CS{:}N.C_2H_5$.

The mustard oils are liquids, almost insoluble in water, and possess a very penetrating odor. They boil at lower temperatures than the isomeric thiocyanic esters.

When heated with hydrochloric acid to 100°, or with H_2O to 200°, they break up into amines, hydrogen sulphide and carbon dioxide:—

$$CS{:}N.C_2H_5 + 2H_2O = CO_2 + SH_2 + NH_2.C_2H_5.$$

On heating with a little dilute sulphuric acid carbon oxysulphide, COS, is formed together with the amine. Nascent hydrogen (zinc and hydrochloric acid) acts as follows:—

$$CS{:}N.C_2H_5 + 2H_2 = CSH_2 + NH_2.C_2H_5.$$

The mustard oils change to urethanes on heating them with absolute alcohol to 100°, or with alcoholic potash. They unite with ammonia and amines, yielding alkylic thio-ureas (see these). Upon boiling their alcoholic solution with HgO or $HgCl_2$, a substitution of oxygen for sulphur occurs, with formation of esters of isocyanic acid. These immediately yield the dialkylic ureas with water (see p. 274).

Methyl Mustard Oil, $CS{:}N.CH_3$, methyl isothiocyanic ester, methyl thiocarbimide. It is a crystalline mass, melting at 34° and boiling at 119°.

Ethyl Mustard Oil, $CS{:}N.C_2H_5$, boils at 133° and has a specific gravity 1.019 at 0°. **Propyl Mustard Oil**, $CS{:}N.C_3H_7$, boils at 153°. **Isopropyl Mustard Oil**, $CS{:}N.C_3H_7$, boils at 137°.

Butyl Mustard Oil, $CS{:}N.C_4H_9$ (with normal butyl), boils at 167. **Isobutyl Mustard Oil**, $CS{:}N.C_4H_9$ (from isobutylamine), boils at 162°; specific gravity 0.9638 at 14°. The mustard oil having the secondary butyl group, $\begin{matrix} C_2H_5 \\ CH_3 \end{matrix}\!\!>\!CH$, occurs in the ethereal oil of *Cochlearea officinalis*. It boils at 159.5°; its specific gravity equals 0.944 at 12°.

Isoamyl Mustard Oil, $CS{:}N.C_5H_{11}$, boils at 183°.

The most important of the mustard oils is the common or—

Allyl Mustard Oil, $CS{:}N.C_3H_5$—Allyl Thiocarbimide. This is the principal constituent of ordinary mustard oil, which is obtained by distilling powdered black mustard seeds (from *Sinapis nigra*). In the latter there is potassium *myronate* (see Glucosides), which in the presence of water, under the influence of a ferment, *myrosin* (also present in the seed), breaks up into grape sugar, primary potassium sulphate and mustard oil:—

$$C_{10}H_{18}KNO_{10}S_2 = C_6H_{12}O_6 + SO_4KH + CS.N.C_3H_5.$$

The reaction occurs even at 0°, and there is a small amount of allyl sulphocyanate produced at the same time.

Mustard oil is artificially prepared by distilling allyl iodide or bromide with alcoholic potassium or silver thiocyanate:—

$$CN.SK + C_3H_5I = CS.N.C_3H_5 + KI;$$

a molecular rearrangement occurs here (p. 279). It may also be obtained by distilling the mercuric chloride of allyl sulphide with potassium sulphocyanide (p. 143).

Pure allyl thiocarbimide is a liquid not readily dissolved by water, and boiling at 150.7°; its specific gravity equals 1.017 at 10°. It has a pungent odor and causes blisters upon the skin. When heated with water or hydrochloric acid the following reaction ensues:—

$$CS{:}N.C_3H_5 + 2H_2O = CO_2 + SH_2 + NH_2.C_3H_5.$$

It unites with aqueous ammonia to allyl thio-urea. When heated with water and lead oxide it yields diallyl urea.

ESTERS OF TRITHIOCYANURIC ACID.

Trithiocyanuric acid corresponds to thiocyanic acid, but thio-isocyanuric acid is not known.

Trithiocyanuric Acid, $C_3N_3(SH)_3$, is formed in the action of cyanuric chloride upon sodium sulphide, and may be obtained from its esters by saponification with sodium sulphide. Acids separate it from its salts in small yellow needles, which decompose but do not melt above 200° C. Its esters result when cyanuric chloride and sodium mercaptides interact, and by the polymerization of the thiocyanic esters, $CN.SR$, when heated to 180° with a little HCl. More HCl causes them to split up into cyanuric acid and mercaptans.

Methyl Trithiocyanuric Ester, $C_3N_3(S.CH_3)_3$, melts at 188° and sublimes with scarcely any decomposition. Heating with ammonia causes a successive replacement of the mercaptan residues by amide groups, the final product being melamine (p. 290):—

$$C_3N_3\left\{\begin{array}{l}(S.CH_3)_2\\ NH_2\end{array}\right., \quad C_3N_3\left\{\begin{array}{l}(S.CH_3)\\ NH_2\\ NH_2\end{array}\right. \text{ and } \underset{\text{Melamine.}}{C_3N_3(NH_2)_3}.$$

The esters react similarly with methylamine and dimethylamine (*Berichte*, 18, 2755).

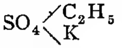
CYANIDES OF THE ALCOHOL RADICALS.

(1) NITRILES.

By this term we understand those derivatives of the alcohol radicals with the cyanogen group, CN, in which the fourth affinity of carbon is linked to the alcohol radicals.

The following general methods serve for their formation:—

1. The distillation of a potassic alkyl sulphate with potassium cyanide:—



$$SO_4\left\langle\begin{matrix}C_2H_5\\ K\end{matrix}\right. + CNK = C_2H_5.CN + SO_4K_2;$$

or by heating the alkylogens with potassium cyanide in alcoholic solution to 100°:—

$$C_2H_5I + CNK = C_2H_5.CN + KI.$$

Isocyanides (p. 287) form in slight amount in the first reaction. For their removal shake the distillate with aqueous hydrochloric acid until the unpleasant odor of the isocyanides has disappeared, then neutralize with soda and dry the nitriles with calcium chloride.

2. The dry distillation of ammonium salts of the acids with P_2O_5, or some other dehydrating agent:—

$$\underset{\text{Ammonium Acetate.}}{CH_3.CO.O.NH_4} - 2H_2O = \underset{\text{Acetonitrile.}}{CH_3.CN.}$$

This method of production explains why these cyanides are termed acid nitriles.

3. By the removal of water from the amides of the acids when these are heated with P_2O_5, P_2S_5—or phosphoric chloride (see amidchlorides, p. 258):—

$$CH_3.CO.NH_2 + PCl_5 = CH_3.CN + POCl_3 + 2HCl,$$
$$5CH_3.CO.NH_2 + P_2S_5 = 5CH_3.CN + P_2O_5 + 5H_2S.$$

The nitriles occur already formed in bone-oils.

The nitriles are liquids, usually insoluble in water, possessing an ethereal odor, and distilling without decomposition. When heated to 100° with water, they break up into acids and ammonia:—

$$CH_3.CN + 2H_2O = CH_3.CO.OH + NH_3.$$

This decomposition is more readily effected on heating with acids or alkalies (p. 211). The acid amides result by the union of the nitriles with 1 molecule of water.

Nascent hydrogen (sodium amalgam) converts them into amines:—

$$CH_3.CN + 2H_2 = CH_3.CH_2.NH_2.$$

This conversion is most easily accomplished by means of metallic sodium and absolute alcohol (p. 159 and *Berichte*, 22, 812).

The nitriles can unite directly with bromine and with the halogen hydrides:—

$$CH_3.CN \quad \text{yields} \quad CH_3.CBr{:}NH \quad \text{and} \quad CH_3.CBr_2.NH_2.$$

These compounds are identical with those formed by the action of PCl_5 upon the amides (p. 258).

The nitriles form thio-amides with H_2S (p. 260):—

$$CH_3.CN + SH_2 = CH_3.CS.NH_2.$$

With monobasic acids and acid anhydrides they yield secondary and tertiary amides (p. 257).

They combine with alcohols and HCl to imido-ethers, $R.C\begin{matrix}\diagup NH\\ \diagdown OR\end{matrix}$ (p. 292); thus, from CNH we get formido-ethers. The nitriles become amidines with ammonia and the amines (p. 293). Hydroxylamine unites with them to form oxamidines, or amidoximes (p. 294). Metallic sodium induces in them peculiar polymerizations; bimolecular cyan-alkyls, like dicyan methyl (p. 284), being formed in ethereal solutions. If, however, sodium acts upon the pure nitriles at a temperature of 150° the products are *cyanalkines* (thus methyl cyanide, C_2H_3N, yields cyanmethine, $C_6H_9N_3$; ethyl cyanide, C_3H_5N, yields cyanethine, $C_9H_{15}N_3$); these were formerly classed as tri-molecular cyanides, but really belong to the pyrimidine or metadiazine bases (see these, and *Berichte*, 22, Ref. 328).

Formonitrile	or	Hydrogen	Cyanide,	$H.CN$
Acetonitrile	"	Methyl	"	$CH_3.CN$
Propionitrile	"	Ethyl	"	$C_2H_5.CN$
Butyronitrile	"	Propyl	"	$C_3H_7.CN$
Valeronitrile	"	Butyl	"	$C_4H_9.CN$, etc.

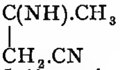
1. **Hydrogen Cyanide,** CNH (p. 265), the lowest member of the series, is to be regarded as **formonitrile,** because it is obtained from ammonium formate by the withdrawal of water:—

$$CHO.O.NH_4 - 2H_2O = CHN.$$

Conversely, on boiling with acids or alkalies it yields formic acid and ammonia. Nascent hydrogen converts it into methylamine, $CH_3.NH_2$.

Acetonitrile, Methyl Cyanide, $CH_3.CN = C_2H_3N$, is best obtained by distilling acetamide with P_2O_5. It is a liquid with an agreeable odor, and boils at 81.6°. It is miscible with water, and burns with a violet light. When boiled with acids or alkalies it yields ammonia and acetic acid. Nascent hydrogen converts it into ethylamine.

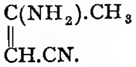
Dicyan-methyl, $C_4H_6N_2$, is obtained by the action of sodium upon an ethereal solution of acetonitrile. It is constituted according to the tautomeric formulas:—



$$\begin{array}{l} C(NH).CH_3 \\ | \\ CH_2.CN \end{array}$$

Imido-acetyl
Cyanmethyl.

or



$$\begin{array}{l} C(NH_2).CH_3 \\ \| \\ CH.CN. \end{array}$$

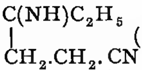
Nitrile of
β-Amidocrotonic Acid.

It crystallizes from ether in colorless needles, melting at 53°. It forms cyanacetone with concentrated hydrochloric acid (*Berichte*, 22, Ref. 325 and 327).

Substituted acetonitriles are obtained from the substituted acetamides by distillation with P_2O_5. $CH_2Cl.CN$ boils at 124°; its specific gravity at 11° equals 1.204. $CHCl_2.CN$ boils at 112°, and its specific gravity is 1.374 at 11°. $CCl_3.CN$ boils at 83°; its specific gravity at 12° is 1.439. The direct chlorination of acetonitrile only occurs in the presence of iodine (*Annalen*, 229, 163.) Trichloroacetonitrile condenses in sunlight to the polymeride, $C_3N_3(CCl_3)_3$, melting at 96°. Boiling potash changes it to chloroform and cyanuric acid.

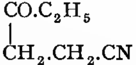
3. **Propionitrile, Ethyl Cyanide,** $C_3H_5N = C_2H_5.CN$. This is also formed by the action of cyanogen chloride and dicyanogen upon zinc ethyl. It is an agreeably smelling liquid, which boils at 98°. Its specific gravity equals 0.787. Salt separates it from its aqueous solution. In all its reactions, it is perfectly analogous to acetonitrile.

Metallic sodium converts ethyl cyanide in ethereal solution into dicyan-ethyl, $C_6H_{10}N_2$. It is probably imido-propionyl-cyanethine,



$$\begin{array}{l} C(NH)C_2H_5 \\ | \\ CH_2.CH_2.CN \end{array}$$

(see above). It is crystalline, melts at 48° and boils at 258°. Acids convert it into propionyl-cyanethine,



$$\begin{array}{l} CO.C_2H_5 \\ | \\ CH_2.CH_2.CN \end{array}$$

(*Berichte*, 22, Ref. 833; 22, Ref. 325). Cyanacetone, $C_9H_{15}N_3 = C_4N_2(CH_3)(C_2H_5)_2(NH_2)$, the amido derivative of methyl-diethyl-pyrimidine (see this), results on heating ethyl cyanide and sodium to 150°.

Chlorine displaces two hydrogen atoms in propionitrile, yielding *a*-dichlorpropionitrile, $CH_3.CCl_2.CN$. This is a liquid, boiling at 103–107°, and upon standing, it polymerizes to the solid $(C_3H_3Cl_2N)_3$. Sodium, or sodium amalgam, effects the same more rapidly. The product crystallizes in plates, which melt at 73.5°, and decompose when heated. Heated with sulphuric acid and water, both compounds yield *a* dichlorpropionic acid, and with alcohol and sulphuric acid its ester (p. 225). When polymeric dichloropropionitrile is reduced with zinc dust it yields cyanur-triethyl (p. 285).

4. **Butyronitrile, Propyl Cyanide,** $C_3H_7.CN$, boils at 118–119°, and has the odor of bitter-almond oil. **Isopropyl Cyanide,** $C_3H_7.CN$, is formed by the prolonged heating of isobutyric acid with potassium thiocyanate. It boils at 107–108°.

5. **Valeronitriles,** $C_5H_9.N = C_4H_9.CN$, **Butyl Cyanides.**

(1) *Normal butyl cyanide* boils at 140–141°; its specific gravity is 0.816 at 0°. (2) *Isobutyl cyanide* boils at 126-128°, and has the odor of oil of bitter almonds; its specific gravity equals 0.8227 at 0°. (3) *Tertiary butyl cyanide* is produced on heating tertiary butyl iodide, $(CH_3)_3CI$, with potassio-mercuric cyanide. It boils at 105–106°, becomes crystalline in the cold, and melts at + 16°.

The following higher nitriles may be easily derived from their respective acid amides by action of P_2O_5 (*Berichte*, 15, 1730): *Lauronitrile*, $C_{12}H_{23}N$(F.P. + 4°); *myristonitrile*, $C_{14}H_{27}N$ (19°); *palmitonitrile*, $C_{16}H_{31}N$ (31°); and *stearonitrile*, $C_{18}H_{35}N$ (41°).

Allyl Cyanide, $C_3H_5.CN = CH_2:CH.CH_2.CN$, is not known. The compound produced by heating allyl iodide with potassium cyanide is the isomeric *Propenyl Cyanide*, $C_3H_5.CN = CH_3.CH:CH.CN$. This results from a molecular rearrangement. It occurs in crude mustard oil.

It is a liquid with an odor resembling that of leeks, boils at 118°, and has a specific gravity of 0.835 at 15°. It combines with bromine to a dibromide, $C_3H_5Br_2.CN$. This becomes a β dibrombutyric acid by saponification (*Berichte*, 22, Ref. 495). It yields nothing but acetic acid when oxidized with a chromic acid mixture. It yields crotonic acid when boiled with alcoholic potash (p. 238).

Tricyanalkyls or **Cyanur-trialkyls.** Although the cyanogen derivatives frequently condense to tricyanogen or cyanuric compounds, yet tricyanhydride, or cyanuric acid, is not known. Its alkyl derivatives exist.

Cyanuric Triethyl, $C_3N_3(C_2H_5)_3$, results from the action of zinc dust upon polymeric α-dichloropropionitrile (p. 284), or zinc dust and acetic acid (*Berichte*, 22, 1446; 20, Ref. 55). It is very volatile, and has a narcotic odor. It melts at 29° and boils at 119°. It is decomposed into propionic acid and ammonia (*Berichte*, 23, 766) by hydrochloric acid at the ordinary temperatures.

A general method for the preparation of diphenylated cyanur-alkyls consists in the action of $AlCl_3$ upon a mixture of benzonitrile and the chlorides of fatty acids. The nitriles of fatty acids do not yield analogous compounds (*Berichte*, 23, 765).

NITRO-DERIVATIVES OF ACETONITRILE.

In this section a class of compounds will be considered which, although not directly obtained from acetonitrile, are yet regarded as derivatives of it (*Berichte*, **16**, 2419).

Nitro-acetonitrile, $C_2H_2N_2O_2 = CH_2(NO_2).CN$, or hypothetical fulminic acid, is considered the basis of the so-called fulminates, derived from it by the introduction of metals for two hydrogen atoms. The influence of the negative groups, CN and NO_2, explains the acid nature of acetonitrile (p. 266).

A compound having the composition of nitro-acetonitrile has been obtained by the action of concentrated sulphuric acid upon ammonium fulminurate. It is a crystalline solid, insoluble in water, melts at 40°, and volatilizes very readily (*Berichte*, 9, 783).

Mercury Fulminate, $C_2HgN_2O_2 = CHg(NO_2).CN(?)$ (*Berichte*, **18**, Ref. 148), is formed by heating a mixture of alcohol, nitric acid and mercuric nitrate.

1 part mercury is dissolved in 12 parts nitric acid (sp. gr. 1.345), 5.5 parts alcohol of 90 per cent. added, and the whole well shaken. After a little time, as soon as energetic reaction commences, 6 parts alcohol more are gradually added. At first metallic mercury separates, but subsequently dissolves and deposits as mercuric fulminate in flakes (*Berichte*, 9, 787). Modifications of this method may be found in *Berichte*, 19, 993 and 1370.

Fulminating mercury crystallizes in shining, gray-colored prisms, which are tolerably soluble in hot water. It explodes violently on percussion and also when acted upon by concentrated sulphuric acid. Hydrogen sulphide precipitates mercuric sulphide from its solution, the liberated fulminic acid immediately breaking up into CO_2 and ammonium thiocyanate. Concentrated hydrochloric acid evolves CO_2 and yields hydroxylamine hydrochloride, a procedure well adapted for the preparation of hydroxylamine (*Berichte*, 19, 993).

Bromine converts mercuric fulminate into *dibromnitroacetonitrile*, $CBr_2(NO_2).CN$, which forms large crystals, soluble in alcohol and ether, and melting at 50°. Iodine produces the iodide, $CI_2(NO_2).CN$; colorless prisms, melting at 86°. Chlorine gas changes mercuric fulminate into $HgCl_2$, CNCl and chloropicrin. Ammonia in aqueous solution decomposes it into urea and guanidine.

On boiling mercury fulminate with water and copper or zinc, metallic mercury is precipitated and copper and zinc fulminates ($C_2CuN_2O_2$ and $C_2ZnN_2O_2$) are produced. Silver fulminate, $C_2Ag_2N_2O_2$, is prepared after the manner of the mercury salt, and resembles the latter. Potassium chloride precipitates from hot silver fulminate one atom of silver as chloride and the double salt, $C_2AgKN_2O_2$, crystallizes from the solution. Nitric acid precipitates from this salt *acid silver fulminate*, $C_2AgHN_2O_2$, a white, insoluble precipitate.

Dinitro-acetonitrile, $CH(NO_2)_2.CN$. Its ammonium salt is produced when hydrogen sulphide acts upon *trinitro-acetonitrile*:—

$$C(NO_2)_3.CN + 4H_2S = C(NH_4)(NO_2)_2.CN + 4S + 2H_2O.$$

Sulphuric acid liberates the nitrile from this salt, and it may be withdrawn from the solution by shaking with ether. It forms large, colorless crystals and conducts itself like a monobasic acid. The silver salt, $C_2Ag(NO_2)_2N$, explodes very violently. It forms $C_2Br(NO_2)_2N$ with bromine.

Trinitro-acetonitrile, $C_2(NO_2)_3N$, is obtained by the action of a mixture of concentrated nitric and sulphuric acids upon potassium fulminate. It separates out as a thick oil, with evolution of CO_2, and on cooling solidifies.

Trinitro-acetonitrile is a white, crystalline, camphor-like mass, melting at 41.5°, and exploding at 200°. It volatilizes at 60° in an air current. Water and alcohol decompose it, even in the cold, into CO_2 and the ammonium salt of nitroform (p. 112).

Fulminuric Acid, $C_3N_3O_3H_3$, or **Isocyanuric Acid**. Its alkali salts are obtained by boiling mercuric fulminate with potassium chloride or ammonium chloride and water. In its preparation 60–75 grams of mercuric fulminate are heated with 60 c.c. of a saturated ammonium chloride solution, and 700–800 c.c. of water, until mercuric oxide no longer separates. The solution will then contain $HgCl_2$ and ammonium fulminurate. Ammonium hydrate is now employed to throw out all the mercury, when the solution is filtered and concentrated to crystallization. To obtain the free acid, add lead acetate to the solution of the ammonium salt, decompose the lead salt with hydrogen sulphide, and evaporate the filtrate down to a small bulk.

Fulminuric acid is an indistinctly crystalline mass, soluble in water, alcohol and ether, and deflagrating at 145°. It is a monobasic acid, yielding finely crystallized alkali salts. Especially characteristic is the *Cuprammonium salt*, $C_3N_3O_3H_2(CuNH_3)$, which precipitates from the aqueous solution of the acid or its alkali salt when boiled with ammoniacal copper sulphate. It consists of glistening dark blue prisms. Mercury fulminurate is produced when mercury fulminate is heated with alcoholic ammonia.

Trinitroacetonitrile is formed by the action of a mixture of concentrated nitric and sulphuric acids upon fulminuric acid:—

$$C_3N_3O_3H_3 + 2NO_3H = C_2(NO_2)_3N + NH_3 + CO_2 + H_2O.$$

The constitution of fulminuric acid is not known. Consult *Berichte*, 19, Ref. 22, upon an isomeric isofulminuric acid.

(2) ISOCYANIDES OR CARBYLAMINES.

These constitute a series of compounds parallel to, and isomeric with, the nitriles or alkylcyanides. They are obtained:—

1. By digesting chloroform and primary amines with alcoholic potash (A. W. Hofmann):—

$$C_2H_5.NH_2 + CCl_3H = C_2H_5.NC + 3HCl.$$

The carbylamine test of Hofmann for detection of primary amines is based on this (p. 162).

2. By action of the alkyl iodides upon silver cyanide (p. 269) (Gautier):—

$$C_2H_5I + NCAg = C_2H_5.NC + AgI.$$

Preparation.—Heat 2 molecules of silver cyanide with 1 molecule of the iodide, diluted with ⅔ volume of ether, in sealed tubes to 130°–140° for several hours. Water and potassium cyanide (½ part) are added to the product (a compound of the isocyanide with silver cyanide) and the whole distilled upon a water bath (*Annalen*, 151, 239).

3. The isonitriles are produced, too, in slight quantity, in the preparation of the nitriles from alkyl sulphates and potassium cyanide (p. 282).

The carbylamines are colorless liquids which can be distilled, and possess an exceedingly disgusting odor. They are sparingly soluble in water, but readily soluble in alcohol and ether.

While, in the nitriles, the carbon of the cyanogen group is firmly attached to the alcohol radicals, and nitrogen splits off readily as NH_3, in all decomposition reactions of the isonitriles nitrogen remains in combination with the alcohol radical. Hence, in the latter we assume the presence of the isomeric *isocyanogen group*, in which nitrogen figures as a pentad:—

$$\underset{\text{Isocyanide.}}{CH_3 - N \equiv C} \quad \text{and} \quad \underset{\text{Cyanide.}}{CH_3 - C \equiv N.}$$

The isocyanides are characterized by their ready decomposition by dilute acids into formic acid and amines:—

$$C_2H_5.NC + 2H_2O = C_2H_5.NH_2 + CH_2O_2.$$

The same decomposition occurs when they are heated with water to 180°. When oxidized by mercuric oxide they become isocyanic esters (p. 274):—

$$C_2H_5.NC + HgO = C_2H_5.N{:}CO + Hg.$$

The isocyanides, like the cyanides, form crystalline compounds with HCl; water decomposes these into formic acid and amine bases (p. 283). They pass into thio-formamides by their union with H_2S (p. 260).

Methyl Isocyanide, $CH_3.NC$, methyl carbylamine, boils at 59° and dissolves in 10 parts of water. When heated with water it decomposes.

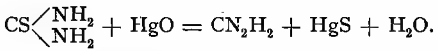
Ethyl Isocyanide, $C_2H_5.NC$, is an oily liquid which swims upon water and boils at 79°.

Isoamyl Isocyanide, $C_5H_{11}.NC$, boils at 137° and swims on water.

Allyl Isocyanide, $C_3H_5.NC$, boils near 106°, and has a specific gravity of 0.796 at 17°.

AMIDE DERIVATIVES OF CYANOGEN.

Cyanamide, $CN.NH_2$, or carbodiimide, $C(NH)_2$, is formed by the action of chlor- or brom-cyan upon an ethereal or aqueous solution of ammonia (*Berichte*, 18, 462), and also by the desulphurizing of thio-urea by means of mercuric chloride or lead peroxide (*Berichte*, 18, 461):—



$$CS\begin{matrix}\diagup NH_2\\ \diagdown NH_2\end{matrix} + HgO = CN_2H_2 + HgS + H_2O.$$

It forms colorless crystals, easily soluble in water, alcohol and ether, and melting at 40°. If heated it polymerizes to dicyandiamide and tricyan-triamide (melamine). It forms salts with strong acids, but these are decomposed by water. Again it unites with metals to salts. An ammoniacal silver nitrate solution throws down a yellow precipitate, CN_2Ag_2, from its solutions. Copper sulphate precipitates black CN_2Cu.

Such metallic compounds are obtained directly by heating the salts of isocyanic acid with the alkaline earths and the heavy metals:—

$$(CO{:}N)_2Ca = CN_2Ca + CO_2.$$

By the action of sulphuric acid or hydrochloric acid, it absorbs water and becomes urea: $CN_2H_2 + H_2O = CO(NH_2)_2$. H_2S converts it into thio-urea, and NH_3 into guanidine (p. 294).

The transpositions and syntheses of cyanamide give no positive evidence as to whether it should be considered as amide, $CN.NH_2$, or carbodiimide, $HN{:}C{:}NH$. Perhaps the forms are tautomeric. However, two isomeric varieties of alkyl derivatives do exist (same as with cyanic acid).

Alkylic Cyanamides are obtained by letting cyanogen chloride act upon primary amines in ethereal solution:—

$$NH_2.CH_3 + CNCl = NH(CH_3).CN + HCl.$$

They may be prepared also by heating the corresponding thio ureas with mercuric oxide and water:—

$$CS\left\langle\begin{matrix}NH.CH_3\\NH_2\end{matrix}\right. + HgO = CN.NH(CH_3) + HgS + H_2O.$$

Methyl Cyanamide, $CN_2H(CH_3)$, and **Ethyl Cyanamide**, $CN_2H(C_2H_5)$, are non-crystallizable thick syrups with neutral reaction. They are readily converted into polymeric isomelamine derivatives.

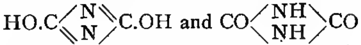
Diethyl Cyanamide, $CN.N(C_2H_5)_2$, is prepared by the interaction of silver cyanamide and ethyl iodide. It is a liquid, boiling at 186–190°. Boiling hydrochloric acid resolves it into CO_2, NH_3 and diethylamine, $NH(C_2H_5)_2$.

Allyl Cyanamide, $CN_2H(C_3H_5)$, called *Sinamine*, is obtained from allylthiourea. It is crystalline and polymerizes readily into triallylmelamine (see below).

Dicyanamide, $NH(CN)_2$, is only known in its salts. The *potassium salt*, C_2N_3K, is obtained by heating potassium cyanide with paracyanogen or with mercuric cyanide (*Berichte*, 13, 2202). It crystallizes in thin needles. Silver nitrate precipitates a white silver salt, C_2N_3Ag, from its solution.

AMIDES OF THE DICYANIC ACIDS.

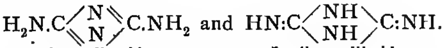
Cyanamide, $CN.NH_2$, may be considered as the *amide* of normal cyanic acid, CN.OH, and carbodi-imide the *imide* of hypothetical isocyanic acid, HN:CO (p. 271). Similarly, there may be derived from the latter acid two isomeric dicyanic acids:—



$$HO.C\left\langle\begin{matrix}N\\N\end{matrix}\right\rangle C.OH \quad\text{and}\quad CO\left\langle\begin{matrix}NH\\NH\end{matrix}\right\rangle CO$$

Normal Dicyanic Acid. Isodicyanic Acid.

and their amide derivatives:—



$$H_2N.C\left\langle\begin{matrix}N\\N\end{matrix}\right\rangle C.NH_2 \quad\text{and}\quad HN:C\left\langle\begin{matrix}NH\\NH\end{matrix}\right\rangle C:NH.$$

Dicyandiamide. Isodicyandiimide.

These are probably tautomeric forms and only isomeric in their alkyl derivatives (not yet known).

Dicyandiamide, $C_2N_4H_4$, Param, results from the polymerization of cyanamide upon long standing or by evaporation of its aqueous solution. It crystallizes in leaflets which melt at 205°. It is insoluble in ether. Its structure probably agrees with the formula, $NH:C\left\langle\begin{matrix}NH_2\\NH.CN.\end{matrix}\right.$ Hence, it can be called cyanguanidine (*Berichte*, 16, 1464; 18, 3106). However, these reactions (together with guanylurea), are explained by the amide or imide formulas (*Berichte*, 19, 2086).

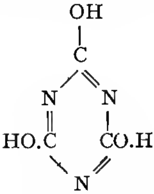
Dicyandiamidine, $C_2H_6N_4O = NH:C\left\langle\begin{matrix}NH_2\\NH.CO.NH_2\end{matrix}\right.$ (guanyl urea), is formed by the action of dilute acids upon dicyandiamide or cyanamide, or by fusing a guanidine salt with urea. It is a strongly basic, crystalline substance, and absorbs

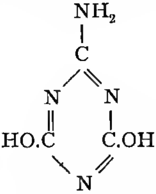
CO_2. When digested with baryta water it decomposes into CO_2, NH_3, and urea (*Berichte*, **20**, 68).

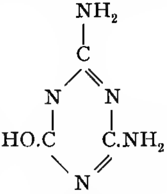
By boiling dicyandiamide with baryta water it is converted into **Amido-dicyanic Acid**, $CO\left\langle\begin{matrix}NH\\NH\end{matrix}\right\rangle C{:}NH$ (?). This crystallizes in needles, and when heated with sulphuric acid changes to biuret.

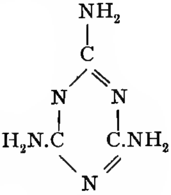
AMIDES OF THE CYANURIC ACIDS.

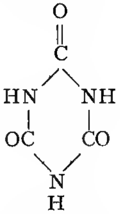
There are also *amide* and *imide* derivatives of the cyanuric acids. These are probably tautomeric and only isomeric in the alkyl compounds:—

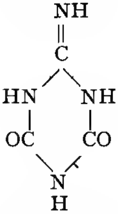

Normal Cyanuric Acid.

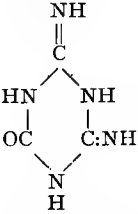

Cyanurmonamide Ammelide.

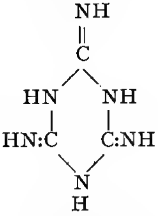

Cyanurdiamide Ammeline.


Cyanurtriamide, Melamine.


Isocyanuric Acid.


Isocyanurmonamide Melanuric Acid.


Isocyanurdiimide Isoammeline.


Isocyanurtriimide Isomelamine.

Melamine, $C_3H_6N_6 = C_3N_3(NH_2)_3$ (see above), Cyanuramide, is produced by:—

The polymerization of cyanamide or dicyandiamide on heating to 150° (together with melam); by heating methyl trithiocyanuric ester to 180° with concentrated ammonia; and by heating cyanuric chloride to 100° with concentrated ammonia:—

$$C_3N_3Cl_3 + 6NH_3 = C_3H_3(NH_2)_3 + 3NH_4Cl.$$

It is obtained from crude melam (p. 291) by extraction with water and precipitation with soda (*Berichte*, **19**, Ref. 345); or more easily from cyanuric chloride (Hofmann, *Berichte*, **18**, 2765).

Melamine is nearly insoluble in alcohol and ether. It crystallizes from hot water in shining monoclinic prisms. It sublimes on heating and decomposes into melam and NH_3. It forms crystalline salts with 1 equivalent of acid.

On boiling with alkalies or acids melamine splits off ammonia and passes successively into *ammeline*, $C_3H_5N_5O = C_3N_3(NH_2)_2.OH$ (a white powder insoluble in water, but soluble in alkalies and mineral acids) (*Berichte*, **21**, Ref. 789); *ammelide*, $C_3H_4N_4O_2 = C_3N_3(NH_2)(OH)_2$, a white powder that forms salts with both acids and bases, and finally cyanuric acid, $C_3N_3(OH)_3$—(*Berichte*, **19**, Ref. 341). Potassium cyanate is directly formed by fusing melamine with KOH.

Melanurenic Acid, $C_3H_4N_4O_2$, from melam and melem (p. 292) when heated with concentrated H_2SO_4 (*Berichte*, 19, Ref. 244), and from dicyandiamide by the addition of CO_2 (on heating $(NH_4)_2CO_3$), is a white amorphous powder, soluble in alkalies and acids with formation of salts, and breaks off into NH_3 and cyanuric acid when boiled with alkalies and acids. It is probably identical with ammelide (*Berichte*, 19, Ref. 341), or it is the isomeric isocyanurimide (*Berichte*, 18, 3106). According to its salts melurenic acid appears to have the doubled formula, $C_6H_8N_8O_4$ (*Berichte*, 19, Ref. 245).

Thioammeline, $C_3H_5N_5S = (CN)_3(NH_2)_2.SH$, is obtained from dicyandiamide by the addition of thiocyanic acid, CN.SH, and from cyanuric chloramide, $C_3N_3(NH_2)_2Cl$, by the action of potassium sulphydrate. It corresponds to ammeline (see above) (*Berichte*, 20, 1059). Its esters result from heating trithiocyanuric esters with ammonia (p. 281).

ALKYL DERIVATIVES OF MELAMINE.

While melamine is only known in one form as cyanurtriamide, two series of isomeric alkyl derivatives exist—obtained from normal melamine and hypothetical isomelamine:—

(1) $C_3N_3(NHR)_3$ and $C_3H_3(NR_2)_3$.	(2) $C_3N_3H_3(NR)_3$.
Normal Alkylmelamines.	Isoalkylmelamines.

These are distinguished from each other not only in the manner of their preparation but also in their transpositions.

(1) **Normal Alkylmelamines** are obtained from the trithiocyanuric esters, $C_3N_3(S.CH_3)_3$, and from cyanuric chloride, $C_3N_3Cl_3$, upon heating with primary and secondary amines (*Berichte*, 18, Ref. 498): $C_3N_3Cl_3 + 3NH(CH_3)_2 = C_3N_3\left(N{CH_3 \atop CH_3}\right)_3 + 3HCl$. Heating with hydrochloric acid causes them to split up into cyanuric acid and the constituent alkylamines.

Trimethylmelamine, $C_3N_3(NH.CH_3)_3$, dissolves readily in water, alcohol and ether. It melts at 115°. **Triethylmelamine**, $C_3N_3(NH.C_2H_5)_3$, crystallizes in needles and melts at 73–74° C.

Hexamethylmelamine, $C_3N_3[N(CH_3)_2]_3$, consists of needles, melting at 171° C. **Hexaethylmelamine**, $C_3H_3[N(C_2H_5)_2]_3$, is a liquid, and is decomposed by hydrochloric acid into cyanuric acid and 3 molecules of diethylamine.

(2) **Alkylisomelamines** are formed by the polymerization of the alkylcyanamides, CN.NHR, upon evaporating their solutions (obtained from the alkylthioureas on warming with mercuric oxide and water). They are crystalline bodies. When heated with hydrochloric acid they yield cyanuric esters and ammonium chloride (*Berichte*, 18, 2784).

Trimethylisomelamine, $C_3N_3H_3(N.CH_3)_3 + 3H_2O$, melts at 179° when anhydrous. It sublimes about 100°. **Triethylisomelamine**, $C_3N_3H_3(N.C_2H_5)_3 + 4H_2O$, consists of very soluble needles. Consult Hofmann, *Berichte*, 18, 3217, for the phenyl derivatives of the mixed melamines (also amide and imide bodies).

COMPLEX CYANAMIDES.

Melam, $C_6H_9N_{11}$. Formed on rapidly heating $CNSNH_4$ or CNSK to 200° with ammonium chloride. Melam and sulphocyan-melamine are produced at the same time. The latter dissolves on boiling with water, while melam and melem constitute the residue, and are separated by alcohol, the first being soluble in this solvent (*Berichte*, 19, Ref. 340). It is a granular powder insoluble in water. Boiling alkalies or acids decompose it into NH_3 and ammeline. Its constitution is, therefore, probably $(NH_2)_2C_3N_3(NH)C_3N_3(NH_2)$(l. c).

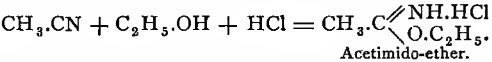
Melem, $C_6H_6N_{10}$ (see above), decomposes on boiling with alkalies or acids into NH_3 and ammelide. Its composition is probably $(NH_2)C_3N_3(NH_2)C_3N_3(NH_2)$.

Mellon, $C_3H_3N_9 = C_3N_3(NH)_3C_3N_3$, is produced on igniting ammonium sulphocyanide, melam, ammeline, etc. Boiling acids decompose it into NH_3 and *cyameluric acid*, $C_6H_3N_7O_3$ (*Berichte*, 19, Ref. 340).

IMIDO-ETHERS, AMIDINES AND OXAMIDINES.

The imido-ethers, the amidines, the oxamidines and guanidine (p. 294) are intimately related to the nitriles and cyanamides.

(1) The **Imido-Ethers**, $R.C\Big\langle\begin{matrix}NH\\OR\end{matrix}$ (their HCl salts), are produced by the action of HCl upon a mixture of a nitrile with an alcohol (in molecular quantities) (Pinner, *Berichte*, 16, 353, 1654):—

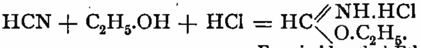


$$CH_3.CN + C_2H_5.OH + HCl = CH_3.C\Big\langle\begin{matrix}NH.HCl\\O.C_2H_5.\end{matrix}$$

Acetimido-ether.

Acetimido-ethyl Ether, when liberated from its HCl-salt by means of NaOH, is a peculiar-smelling liquid, boiling at 97°. Its HCl-salt crystallizes in shining leaflets, and like the other imido-ethers is readily decomposed by heat (with formation of acetamide and ethyl chloride).

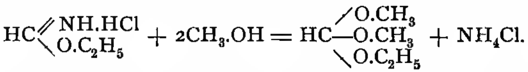
The *formimido-ethers* are obtained from CNH, alcohol and HCl by a reaction analogous to that given above:—



$$HCN + C_2H_5.OH + HCl = HC\Big\langle\begin{matrix}NH.HCl\\O.C_2H_5.\end{matrix}$$

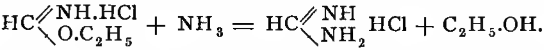
Formimido-ethyl Ether.

These are only known in their salts, which suffer various noteworthy transformations. Upon standing with alcohols they pass into esters of orthoformic acid (see this):—



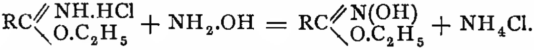
$$HC\Big\langle\begin{matrix}NH.HCl\\O.C_2H_5\end{matrix} + 2CH_3.OH = HC\begin{matrix}/O.CH_3\\—O.CH_3\\\backslash O.C_2H_5\end{matrix} + NH_4Cl.$$

They yield amidines with ammonia and amines (primary and secondary):—



$$HC\Big\langle\begin{matrix}NH.HCl\\O.C_2H_5\end{matrix} + NH_3 = HC\Big\langle\begin{matrix}NH\\NH_2\end{matrix}HCl + C_2H_5.OH.$$

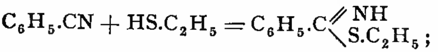
All the other imido ethers react similarly. With hydroxylamine they yield the *acidoximes* (*Berichte*, 17, 185), corresponding to the aldoximes and acetoximes:—



$$RC\Big\langle\begin{matrix}NH.HCl\\O.C_2H_5\end{matrix} + NH_2.OH = RC\Big\langle\begin{matrix}N(OH)\\O.C_2H_5\end{matrix} + NH_4Cl.$$

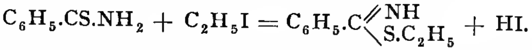
See *Berichte*, 17, 2002, for the phenylhydrazine derivatives of the imido-ethers.

The *imido-thio-ethers* correspond to the imido-ethers. They are obtained by the action of HCl upon nitriles (of the benzene series), and mercaptans:—



$$\mathrm{C_6H_5.CN + HS.C_2H_5 = C_6H_5.C}\begin{array}{l}/\!\!/\mathrm{NH}\\ \backslash\mathrm{S.C_2H_5}\end{array};$$

further, when the *thio-amides* (of the benzene series) are treated with alkyl-iodides (*Berichte*, 15, 564):—



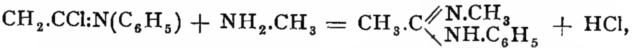
$$\mathrm{C_6H_5.CS.NH_2 + C_2H_5I = C_6H_5.C}\begin{array}{l}/\!\!/\mathrm{NH}\\ \backslash\mathrm{S.C_2H_5}\end{array} + \mathrm{HI}.$$

This class of compounds has a constitution similar to that of the isothioamides (p. 260).

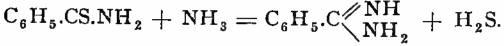
---

(2) The **amidines**, $\mathrm{R.C}\begin{array}{l}/\!\!/\mathrm{NH}\\ \backslash\mathrm{NH_2}\end{array}$, whose hydrogen atoms can be replaced by alkyls, are produced:—

1. From the imid-chlorides, thio-amides, and isothio-amides (p. 255) (*Berichte*, 16, 146), by the action of ammonia or amines (primary and secondary):—

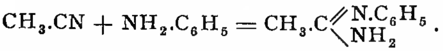


$$\mathrm{CH_2.CCl{:}N(C_6H_5) + NH_2.CH_3 = CH_3.C}\begin{array}{l}/\!\!/\mathrm{N.CH_3}\\ \backslash\mathrm{NH.C_6H_5}\end{array} + \mathrm{HCl},$$



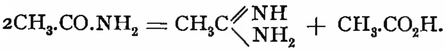
$$\mathrm{C_6H_5.CS.NH_2 + NH_3 = C_6H_5.C}\begin{array}{l}/\!\!/\mathrm{NH}\\ \backslash\mathrm{NH_2}\end{array} + \mathrm{H_2S}.$$

2. From the nitriles by heating them with ammonium chloride, or HCl-amines:—



$$\mathrm{CH_3.CN + NH_2.C_6H_5 = CH_3.C}\begin{array}{l}/\!\!/\mathrm{N.C_6H_5}\\ \backslash\mathrm{NH_2}\end{array}.$$

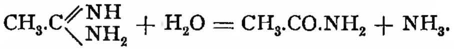
3. From the amides of the acids when treated with HCl (*Berichte*, 15, 208):—



$$\mathrm{2CH_3.CO.NH_2 = CH_3C}\begin{array}{l}/\!\!/\mathrm{NH}\\ \backslash\mathrm{NH_2}\end{array} + \mathrm{CH_3.CO_2H}.$$

4. From the imido-ethers (p. 292) when acted upon with ammonia and amines (*Berichte*, 16, 1647; 17, 179).

The amidines are mono-acid bases. In a free condition they are quite unstable. The action of various reagents on them induces water absorption, the imid-group splits off, and acids or amides of the acids are regenerated:—



$$\mathrm{CH_3.C}\begin{array}{l}/\!\!/\mathrm{NH}\\ \backslash\mathrm{NH_2}\end{array} + \mathrm{H_2O = CH_3.CO.NH_2 + NH_3}.$$

H_2S causes the elimination of the imid- or amid-group from the amidines, and thus converts them into thio-amides (p. 260). CS_2 effects the same, sulpho-cyanic acid, CNSH, and mustard oils, CS.NR, being simultaneously produced (*Annalen*, 192, 30). Hydroxylamine supplants the imid-group in them with the oximid-group, N.OH, with formation of oxamidines, or amidoximes (see these).

Aceto-acetic ester, or acetic anhydride (*Berichte*, 22, 1600), converts the amidines into pyrimidines or metadiazine derivatives (see these). They also combine with phenyl cyanates, with diazo compounds, with chloral, and other aldehydes (see benzamidine, and *Berichte*, 22, 1607).

Formamidine, $\mathrm{CN_2H_4 = CH}\begin{array}{l}/\!\!/\mathrm{NH}\\ \backslash\mathrm{NH_2}\end{array}$ (**Methenylamidine**), is only known in its salts. The HCl-salt, $CN_2H_4.HCl$, is obtained from $CNH.HCl$ (p. 267) on heating it with alcohol:—

$$2CNH.HCl + 2C_2H_5.OH = CN_2H_4.HCl + C_2H_5Cl + CHO_2.C_2H_5.$$

It consists of very hygroscopic needles, melting at 81°, and is decomposed into NH_3 and formic acid by the alkalies.

Acetamidine, $C_2H_6N_2 = CH_3.C\begin{array}{l}\diagup\!\!\diagup NH\\ \diagdown NH_2\end{array}$ **(Acediamine),** is obtained by heating acetamide in a stream of HCl. Its hydrochloric acid salt crystallizes in large, shining prisms that melt at 165°. The acetamidine, separated by alkalies, reacts strongly alkaline and readily breaks up into NH_3 and acetic acid. The higher amidines and their alkyl derivatives are easily obtained by the usual methods (*Berichte*, 17, 178).

The so-called anhydro-bases and ethenyl derivatives of the benzene series (see these) are classed with the amidines.

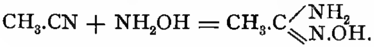
Methenyl-amidoxime, $CH_4N_2O = CH\begin{array}{l}\diagup NH_2\\ \diagdown\!\!\diagdown N.OH\end{array}$ **(Isuretine),** is isomeric with urea, $CO(NH_2)_2$.

It appears on evaporating the alcoholic solution of hydroxylamine and hydrogen cyanide. It crystallizes in rhombic prisms, similar to those of urea, and melts with partial decomposition at 104°–105°. It reacts alkaline and forms crystalline salts with 1 equivalent of the acids. On heating the solutions of its salts, the latter decompose into formic acid, ammonia and hydroxylamine.

Ethenyl-amidoxime, $C_2H_6N_2O = CH_3.C\begin{array}{l}\diagup NH_2\\ \diagdown\!\!\diagdown N.OH\end{array}$, from acetonitrile and hydroxylamine, is very soluble in water, crystallizes in needles, and melts at 135°. Warm water breaks it up into $H_2N.OH$ and acetamide. Acid anhydrides or chlorides convert the amidoximes into *azoximes* (*Berichte*, 18, 1062; see Benzenyl amidoxime).

(3) **Oxamidines,** or **Amidoximes,** $R.C\begin{array}{l}\diagup N.OH\\ \diagdown\!\!\diagdown NH_2\end{array}$. These may be considered amidines, in which one H-atom of the amid- or imid-groups is replaced by hydroxyl. They arise:—

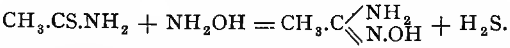
1. From the action of hydroxylamine upon amidines.
2. By the addition of hydroxylamine to the nitriles (*Berichte*, 17, 2746):—



$$CH_3.CN + NH_2OH = CH_3.C\begin{array}{l}\diagup NH_2\\ \diagdown\!\!\diagdown N.OH.\end{array}$$

Acetonitrile. Ethenylamidoxime.

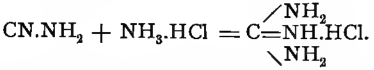
3. From the addition of hydroxylamine to thio-amides (*Berichte*, 19, 1668):—



$$CH_3.CS.NH_2 + NH_2OH = CH_3.C\begin{array}{l}\diagup NH_2\\ \diagdown\!\!\diagdown N.OH\end{array} + H_2S.$$

The amidoximes are crystalline, very unstable bodies, which readily break up into hydroxylamine and acid amides or acids.

Guanidine, $CN_3H_5 = HN{:}C\begin{array}{l}\diagup NH_2\\ \diagdown NH_2,\end{array}$ carb-diamid-imide, is an amidine of carbonic acid. It may also be considered as urea, $CO(NH_2)_2$, in which the oxygen has been replaced by the imid-group. It was first obtained by the oxidation of guanine with hydrochloric acid and potassium chlorate, hence its name. It is formed synthetically by heating cyanogen iodide and NH^3, and from cyanamide (p. 289) and ammonium chloride in alcoholic solution at 100°:—

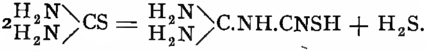


$$CN.NH_2 + NH_3.HCl = C\begin{matrix}\diagup NH_2\\ =NH.HCl.\\ \diagdown NH_2\end{matrix}$$

This is analogous to the formation of formamidine from HCN. It is also produced by heating chloropicrin or esters of orthocarbonic acid, with aqueous ammonia, to 150°:—

$$CCl_3(NO_2) + 3NH_3 = CN_3H_5.HCl + 2HCl + NO_2H.$$

It is most readily prepared from the sulphocyanate salt, which is made by prolonged heating of ammonium sulphocyanate to 180°–190°, and the further transposition of the thio urea that forms at first:—



$$2\begin{matrix}H_2N\diagdown\\ H_2N\diagup\end{matrix}CS = \begin{matrix}H_2N\diagdown\\ H_2N\diagup\end{matrix}C.NH.CNSH + H_2S.$$

To get the free guanidine from this salt, evaporate the aqueous solution with an equivalent quantity of potassium carbonate, extract the potassium thiocyanate from the mass with boiling alcohol, and convert the residual guanidine carbonate into sulphate, and from this liberate the guanidine by means of baryta (*Berichte*, 7, 92).

The crystals of guanidine are very soluble in water and alcohol, and deliquesce on exposure. It is a strong base, absorbing CO_2 from the air and yielding crystalline salts with 1 equivalent of the acids. The nitrate, $CN_3H_5.HNO_3$, consists of large scales, which are sparingly soluble in water. The HCl-salt, $CN_3H_5.HCl$, yields a platinum double salt, crystallizing in yellow needles. The carbonate, $(CN_3H_5)_2.H_2CO_3$, consists of quadratic prisms, and reacts alkaline. The sulphocyanate, $CN_3H_5.HSCN$, crystallizes in large leaflets, that melt at 118°.

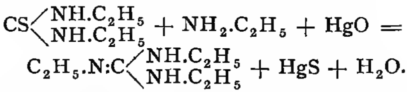
Guanidine is most readily detected by converting it into guanyl urea (p. 289) (*Berichte*, 20, 71).

The *substituted guanidines*, resulting from the introduction of alcohol radicals, are obtained by reactions analogous to those employed in the preparation of guanidine, viz., the heating of cyanamide with the HCl-salts of the primary amines:—

$$CN.NH_2 + NH_2(CH_3).HCl = CN_6H_4(CH_3).HCl.$$

Methyl Guanidine, $CN_3H_4(CH_3)$. Silver oxide separates this from the HCl-salt. It forms a deliquescent, crystalline mass. Its salts with 1 equivalent of acid crystallize quite well. It is also produced on boiling creatine with mercuric oxide and water.

Triethyl Guanidine, $CN_3H_2(C_2H_5)_3$, is obtained by boiling diethyl thio-urea and ethylamine in alcoholic solution with mercuric oxide whereby sulphur is directly replaced by the imid-group (see thio-ureas):—



$$CS\Big\langle\begin{matrix}NH.C_2H_5\\NH.C_2H_5\end{matrix} + NH_2.C_2H_5 + HgO = C_2H_5.N:C\Big\langle\begin{matrix}NH.C_2H_5\\NH.C_2H_5\end{matrix} + HgS + H_2O.$$

Vice versa, the alkylic guanidines, when heated with CS_2, have their imid-group replaced by sulphur (same as with the amidines, p. 293), with formation of thio-ureas.

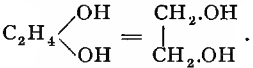
The guanidine-benzene derivatives are especially numerous. Acid residues may also replace the hydrogen of guanidine; these derivatives will receive attention when the urea compounds are described.

Guanidine also forms salts with the fatty acids. When these are heated to 220–230°, water and ammonia break off, and the **guanamines** result. These are produced by the union of 1 molecule of acid and 2 molecules of guanidine. They are mono-acids, and very probably have a structure similar to that of the amidines p. 293). *Formo-guanamine,* $C_3H_5N_5$, from guanidine formate, *aceto-guanamine,* $C_4H_7N_5$, from the acetate, *propio-guanamine,* $C_5H_9N_5$, *butyro-* and *isobutyro-guanamine,* $C_6H_{11}N_5$, etc., (*Berichte,* 9, 454) belong here.

DIVALENT COMPOUNDS.

The introduction of *two* monovalent groups into the hydrocarbons for two hydrogen atoms produces the divalent compounds.

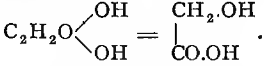
The replacement of hydrogen by two hydroxyl groups yields the divalent *alcohols or glycols,* which we can also term dialcohols (see p. 114):—



$$C_2H_4\Big\langle\begin{matrix}OH\\OH\end{matrix} = \begin{matrix}CH_2.OH\\|\\CH_2.OH\end{matrix}.$$

Ethylene Glycol.

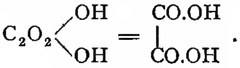
By replacing two hydrogen atoms in the glycols by oxygen, we get the *divalent* (dihydric) *monobasic acids,* containing one carboxyl and one hydroxyl group:—



$$C_2H_2O\Big\langle\begin{matrix}OH\\OH\end{matrix} = \begin{matrix}CH_2.OH\\|\\CO.OH\end{matrix}.$$

Glycollic Acid.

The substitution of two additional hydrogen atoms by oxygen yields the *divalent, dibasic acids,* with two carboxyl groups:—



$$C_2O_2\Big\langle\begin{matrix}OH\\OH\end{matrix} = \begin{matrix}CO.OH\\|\\CO.OH\end{matrix}.$$

Oxalic Acid.

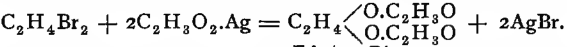
Numerous related derivatives attach themselves to these three principal groups of divalent compounds.

The divalent compounds contain either two similar reactive atomic groups, like the dialdehydes (glyoxal), the diketones (diacetyl), the diamines (ethylene diamine), etc., and hence manifest the typical properties of the monovalent compounds doubly, or they contain two different typical atomic groups, present in the same molecule, and thus present simultaneously the typical characters of different groups of compounds. Derivatives possessed of this mixed function are in addition to the oxyacids or alcohol-acids (see above): the aldehyde alcohols (glycol aldehyde, $CH_2(OH).CHO$), the ketone alcohols (acetyl carbinol, $CH_3.CO.CH_2.OH$), the aldehyde acids (glyoxylic acid), the ketonic acids, the amido-acids, etc.

DIVALENT (DIHYDRIC) ALCOHOLS OR GLYCOLS.

Würtz obtained the glycols in 1856, from the haloid compounds of the alkylens, C_nH_{2n}. They are formed as follows:—

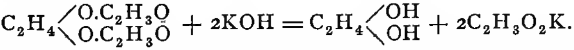
1. By heating the alkylen haloids (p. 100) with silver acetate (and glacial acetic acid), or with potassium acetate in alcoholic solution:—



$$C_2H_4Br_2 + 2C_2H_3O_2.Ag = C_2H_4\left\langle\begin{matrix}O.C_2H_3O\\O.C_2H_3O\end{matrix}\right. + 2AgBr.$$

Ethylene Diacetate.

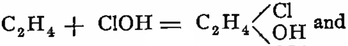
The resulting acetic esters are purified by distillation, and then saponified by KOH:—



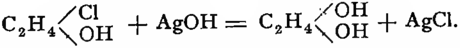
$$C_2H_4\left\langle\begin{matrix}O.C_2H_3O\\O.C_2H_3O\end{matrix}\right. + 2KOH = C_2H_4\left\langle\begin{matrix}OH\\OH\end{matrix}\right. + 2C_2H_3O_2K.$$

Generally in using potassium acetate, a mixture of di-acetate and mono-acetate is produced with free glycol. The mixture is saponified with KOH, or $Ba(OH)_2$. A direct conversion of alkylen haloids into glycols may be attained by heating them with water and lead oxide, or sodium and potassium carbonate (p. 119). When ethylene bromide is heated for some time with much water above 100° it is completely changed to ethylene glycol, whereas with little water aldehyde results (*Annalen*, 186, 393).

2. Another procedure consists in shaking the alkylens, C_nH_{2n}, with aqueous hypochlorous acid, and afterwards decomposing the chlorhydrins formed with moist silver oxide:—



$$C_2H_4 + ClOH = C_2H_4\left\langle\begin{matrix}Cl\\OH\end{matrix}\right. \text{ and}$$

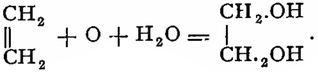


$$C_2H_4\left\langle\begin{matrix}Cl\\OH\end{matrix}\right. + AgOH = C_2H_4\left\langle\begin{matrix}OH\\OH\end{matrix}\right. + AgCl.$$

The glycols appear in small quantities when hydrogen peroxide acts on the olefines C_nH_{2n}:—

$$C_2H_4 + H_2O_2 = C_2H_4(OH)_2.$$

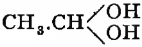
3. By the oxidation of the olefines in alkaline solution (p. 82 and *Berichte*, 21, 1230) with potassium permanganate:—



$$\begin{matrix}CH_2\\ \|\\ CH_2\end{matrix} + O + H_2O = \begin{matrix}CH_2.OH\\ |\\ CH._2OH\end{matrix}.$$

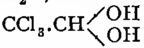
Isobutylene, $(CH_3)_2C{:}CH$, yields isobutylene glycol, $(CH_3)_2C(OH).CH_2.OH$, etc.

From the method of producing glycols out of the alkylens, C_2H_{2n}, by means of their addition products, it would appear that in the glycols the hydroxyl groups are bound to *two different* carbon atoms. *One* carbon atom can link but *one* OH group. Thus from ethidene chloride, $CH_3.CHCl_2$, we cannot obtain the corresponding glycol, $CH_3.CH(OH)_2$. When dihydroxides do form, water separates and the corresponding anhydrides—the aldehydes (p. 188)—result:—

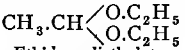


$$CH_3.CH\langle\begin{smallmatrix}OH\\ OH\end{smallmatrix} \text{ yields } CH_3.CHO + H_2O.$$

The union of two OH groups to one carbon atom is more stable if the neighboring carbon atom be attached to negative elements. Thus the rather stable hydrate of chloral, $CCl_3.CHO + H_2O$, can be viewed as a dihydroxyl derivative (as trichlorethidene glycol), $CCl_3.CH\langle\begin{smallmatrix}OH\\ OH\end{smallmatrix}$ (compare glyoxylic and mesoxalic acids). Such hydroxyl groups are usually not capable of further exchange, as is the case with those in the glycols.



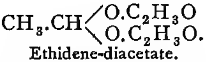
While, therefore, the union of two hydroxyl groups to one carbon atom is but feeble, two oxygen atoms may be firmly attached, if they are linked at the same time with alcoholic or acid radicals, as in—



$$CH_3.CH\langle\begin{smallmatrix}O.C_2H_5\\ O.C_2H_5\end{smallmatrix}$$

Ethidene-diethylate.

and



$$CH_3.CH\langle\begin{smallmatrix}O.C_2H_3O\\ O.C_2H_3O.\end{smallmatrix}$$

Ethidene-diacetate.

The possible isomerisms for the glycols are deduced from the corresponding hydrocarbons, according to the ordinary rules, with the single limitation that but one OH group can be attached to each carbon atom. Thus two glycols, $C_3H_6(OH)_2$, are derived from propane:—

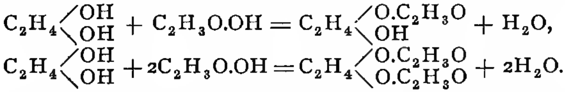
$CH_3.CH(OH).CH_2.OH$ and $CH_2(OH).CH_2.CH_2.OH$.

α-Propylene Glycol. β-Propylene Glycol.

The first contains both a primary and a secondary alcohol group (p. 118), and therefore can be called *primary-secondary glycol;* the second has two primary alcoholic groups, and represents a *di-primary glycol,* etc. The higher glycols are similarly named.

The glycols are neutral, thick liquids, holding, as far as their properties are concerned, a place intermediate between the monohydric alcohols and trihydric glycerol. The solubility of a compound in water increases according to the accumulation of OH groups in it, and it will be correspondingly less soluble in alcohol, and especially in ether. There will be also an appreciable rise in the boiling temperature, while the body acquires at the same time a sweet taste, inasmuch as there occurs a gradual transition from the hydrocarbons to the sugars. In accord with this, the glycols have a sweetish taste, are very easily soluble in water, slightly soluble in ether, and boil much higher (about 100°) than the corresponding monohydric alcohols.

The hydrogen of the hydroxyls may be replaced by the alkali metals (with formation of metallic glycollates, p. 126), and by acid and alcohol radicals. The acid esters are produced by the action of the salts of the fatty acids upon haloid compounds of the alkylens, or even when the free acids act on the glycols (p. 250);—

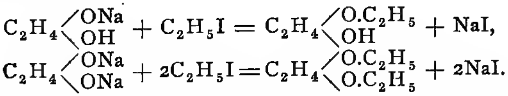


$$C_2H_4\left\langle\begin{matrix}OH\\OH\end{matrix}\right. + C_2H_3O.OH = C_2H_4\left\langle\begin{matrix}O.C_2H_3O\\OH\end{matrix}\right. + H_2O,$$

$$C_2H_4\left\langle\begin{matrix}OH\\OH\end{matrix}\right. + 2C_2H_3O.OH = C_2H_4\left\langle\begin{matrix}O.C_2H_3O\\O.C_2H_3O\end{matrix}\right. + 2H_2O.$$

The formation of acid esters is an excellent means of proving the number of hydroxyl groups present in the polyvalent alcohols (the glycerols—sugars and the phenols). The benzoic esters are especially easy of production by merely shaking the substance under examination with benzene chloride and sodium hydroxide (*Berichte*, 21, 2744; 22, Refs. 668 and 817). The nitric acid esters are also quite well adapted to this purpose, and also the carbaminic esters, through the action of isocyanic acid esters (p. 273), more especially phenylisocyanic ester (see this).

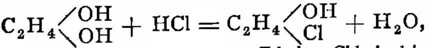
The *alcohol-ethers* are obtained from the metallic glycollates by the action of the alkyl iodides:—



$$C_2H_4\left\langle\begin{matrix}ONa\\OH\end{matrix}\right. + C_2H_5I = C_2H_4\left\langle\begin{matrix}O.C_2H_5\\OH\end{matrix}\right. + NaI,$$

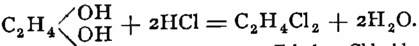
$$C_2H_4\left\langle\begin{matrix}ONa\\ONa\end{matrix}\right. + 2C_2H_5I = C_2H_4\left\langle\begin{matrix}O.C_2H_5\\O.C_2H_5\end{matrix}\right. + 2NaI.$$

When the glycols are treated with hydrochloric and hydrobromic acid, the primary and secondary *haloid esters* (p. 124) are produced. The former are also called chlor- and brom-hydrins, while the latter represent the halogen compounds of the alkylens:—



$$C_2H_4\left\langle\begin{matrix}OH\\OH\end{matrix}\right. + HCl = C_2H_4\left\langle\begin{matrix}OH\\Cl\end{matrix}\right. + H_2O,$$

Ethylene Chlorhydrin.

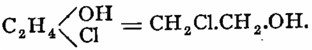


$$C_2H_4\left\langle\begin{matrix}OH\\OH\end{matrix}\right. + 2HCl = C_2H_4Cl_2 + 2H_2O.$$

Ethylene Chloride.

When heated with HI, a more extensive reaction occurs (p. 98).

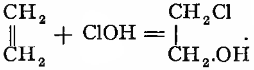
The primary haloid esters can also be considered as substitution products of the monohydric alcohols:—



$$C_2H_4\left\langle\begin{matrix}OH\\Cl\end{matrix}\right. = CH_2Cl.CH_2.OH.$$

Glycol Chlorhydrin. Chlor-ethyl Alcohol.

They can be obtained, too, by the direct addition of hypochlorous acid to the alkylens:—



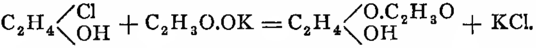
$$\begin{array}{l}CH_2\\ \Vert\\ CH_2\end{array} + ClOH = \begin{array}{l}CH_2Cl\\ \vert\\ CH_2.OH\end{array}.$$

The hypochlorous acid is prepared by acting with chlorine upon HgO suspended in water, or by saturating a dilute and cold solution of NaOH with the gas (*Berichte*, 18, 1767), or by the addition of an excess of boric acid to a solution of chloride of lime (*Berichte*, 18, 2287).

Nascent hydrogen converts them into monohydric alcohols:—

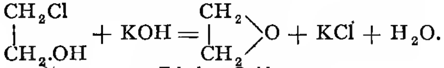
$$C_2H_4Cl.OH + H_2 = C_2H_5.OH + HCl.$$

When they are digested with salts they form primary esters:—



$$C_2H_4\begin{cases}Cl\\ OH\end{cases} + C_2H_3O.OK = C_2H_4\begin{cases}O.C_2H_3O\\ OH\end{cases} + KCl.$$

By treating the haloidhydrins with alkalies we obtain the *anhydrides* of the glycols or *alkylen oxides*:—

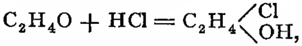


$$\begin{array}{l}CH_2Cl\\ \vert\\ CH_2.OH\end{array} + KOH = \begin{array}{l}CH_2\\ \vert\\ CH_2\end{array}\!\!>O + KCl + H_2O.$$

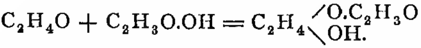
Ethylene Oxide.

This is the only method of forming the α-alkylen oxides (those in which the O-atoms are in union with adjacent C-atoms), whereas the γ- and δ-alkylen oxides (those in which the second union occurs in the γ- or δ-position with reference to the first) can be obtained from the corresponding glycols by direct withdrawal of water when heated alone or upon boiling with 50% sulphuric acid (*Berichte*, 18, 3285; 19, 2843). The α-glycols, under like treatment, yield either unsaturated alcohols, aldehydes or pinacolines, depending upon their constitution (p. 310).

Such oxides, having the oxygen attached to two carbon atoms, are isomeric with the aldehydes and ketones, and boil at lower temperatures than the latter. Notwithstanding they show neutral reaction, they yet possess a strong basic character, precipitating metallic hydroxides from solutions of metallic salts and uniting with acids to form primary esters of the glycols:—

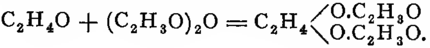


$$C_2H_4O + HCl = C_2H_4\begin{cases}Cl\\ OH,\end{cases}$$



$$C_2H_4O + C_2H_3O.OH = C_2H_4\begin{cases}O.C_2H_3O\\ OH.\end{cases}$$

With the acid anhydrides they yield secondary esters of the glycols:—



$$C_2H_4O + (C_2H_3O)_2O = C_2H_4\begin{cases}O.C_2H_3O\\ O.C_2H_3O.\end{cases}$$

The alkylen oxides are readily soluble in water (distinction from alkyl oxides or esters). When the α-alkylen oxides are heated with water the glycols are regenerated. This is not the case with the γ- and δ-glycols. It is also true that only the α-alkylen oxides form hydramines with ammonia (p. 314). All alkylen oxides unite with hydrochloric acid to form chlorhydrins.

Like the monohydric alcohols, the glycols also form sulphur compounds, amines and sulphonic acids.

Methylene Derivatives.

Methylene Glycol, $CH_2(OH)_2$, is not known and cannot exist (p. 298). Wherever it should occur it eliminates water and yields methylene oxide (*i. e.*, formaldehyde), and trioxymethylene (p. 188). Its ethers and esters have been prepared.

Methylene Diacetic Ester, $CH_2(O.C_2H_3O)_2$, is produced on heating methylene iodide with silver acetate. An oily liquid, insoluble in water and boiling at 170°. Boiling alcohols saponify it, but instead of yielding the expected methylene glycol, trioxymethylene is produced.

Methylene Dimethyl Ether, $CH_2(O.CH_3)_2$, *Methylal* or *Formal*, is obtained in the oxidation of methyl alcohol with MnO_2 and sulphuric acid. It is an ethereal liquid of specific gravity 0.855, and boils at 42°. It is miscible with alcohol and ether, and dissolves in 3 parts water. The *diethyl ether*, $CH_2(O.C_2H_5)_2$, is prepared by the action of sodium ethylate upon methylene chloride, or iodide, and by distilling trioxmethylene with alcohol and sulphuric acid. It boils at 89° (82°). Its specific gravity is 0.8275 at 17°. Consult *Berichte*, 20, 553 for the higher methylals.

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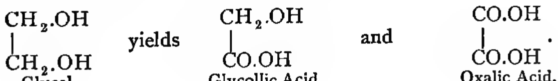
1. Ethylene Glycol, $C_2H_6O_2 = C_2H_4(OH)_2$.

This is a colorless, thick liquid, with a specific gravity of 1.125 at 0°, and boiling at 197.5°. It solidifies when exposed to low temperatures, and melts at — 11.5°. It is miscible with water and alcohol. Ether dissolves but small quantities of it.

Preparation.—Heat a mixture of 195 grams ethylene bromide (1 molecule), 102 grams potassium acetate (2 molecules) and 200 grams alcohol, of 90 per cent., until all the ethylene bromide is dissolved, then filter off the potassium bromide and fractionate the filtrate (*Demole*). 2. Boil 188 grams ethylene bromide, 133 grams K_2CO_3 and 1 litre of water, until all the ethylene bromide is dissolved (*Annalen*, 192, 240 and 250).

On heating ethylene glycol with zinc chloride water is eliminated and acetaldehyde (and crotonaldehyde) (p. 199) formed. Nitric acid oxidizes glycol to glycollic and oxalic acids :—



$$\begin{matrix}CH_2.OH\\ |\\ CH_2.OH\end{matrix} \quad \text{yields} \quad \begin{matrix}CH_2.OH\\ |\\ CO.OH\end{matrix} \quad \text{and} \quad \begin{matrix}CO.OH\\ |\\ CO.OH\end{matrix}.$$

Glycol. Glycollic Acid. Oxalic Acid.

The following aldehyde-compounds are produced at the same time:—

$$\begin{array}{c}CHO\\ |\\ CHO\end{array} \text{ and } \begin{array}{c}CHO\\ |\\ CO.OH.\end{array}$$

Glyoxal. Glyoxylic Acid.

And when glycol is heated, together with caustic potash, to 250°, it is oxidized to oxalic acid with evolution of hydrogen.

Heated to 200° with concentrated hydrochloric acid, glycol is converted into ethylene chloride, $C_2H_4Cl_2$.

Metallic sodium dissolves in glycol, forming sodium mono-ethylenate $C_2H_4{<}\genfrac{}{}{0pt}{}{OH}{ONa}$, and (at 170°) disodium ethylenate, $C_2H_4(ONa)_2$. Both are white, crystalline bodies, regenerating glycols with water. The alkylogens convert them into ethers.

Ethylene Ethyl Ether, $C_2H_4{<}\genfrac{}{}{0pt}{}{OH}{O.C_2H_5}$, is formed by the union of ethylene oxide with ethyl alcohol. A pleasantly smelling liquid, boiling at 127°.

Ethylene Diethyl Ether, $C_2H_4(O.C_2H_5)_2$, is insoluble in water, and boils at 123°.

The following acid esters have been made:—

Glycol Mono-acetate, $C_2H_4{<}\genfrac{}{}{0pt}{}{O.C_2H_3O}{OH}$, boils at 182°, and is miscible with water.

If hydrochloric acid gas be conducted into the warmed solution, **glycol chloracetin,** $C_2H_4{<}\genfrac{}{}{0pt}{}{O.C_2H_3O}{Cl}$, or chlorinated acetic ethyl ester, $CH_2Cl.CH_2.O.C_2H_3O$, is produced. This boils at 144°.

Glycol Diacetate, $C_2H_4(O.C_2H_3O)_2$, is obtained by heating ethylene bromide with silver acetate. A liquid of specific gravity 1.128 at 0°, and boiling at 186°. It is soluble in 7 parts water.

Glycol or Ethylene Chlorhydrin, $CH_2.Cl.CH_2.OH$(p. 299), is formed by heating glycol to 160°, and conducting HCl through it, or by the addition of ClOH to C_2H_4. It is a liquid, boiling at 128°, and is miscible with water. A chromic acid mixture oxidizes it to monochlor-acetic acid, $CH_2Cl.CO_2H$. **Ethylene bromhydrin,** $C_2H_4Br.OH$, is not very soluble in water, and boils at 147°; its specific gravity at 0° equals 1.66. When chlorhydrin is heated with potassium iodide we get **glycol iodhydrin,** $C_2H_4I.OH$. This is a thick liquid, which decomposes when distilled.

Glycol or Ethylene- hydroxy-sulphuric Acid, $C_2H_4{<}\genfrac{}{}{0pt}{}{OH}{O.SO_2.OH}$, is produced on heating glycol with sulphuric acid. It is perfectly similar to ethyl sulphuric acid (p. 150), and decomposes, when boiled with water or alkalies, into glycol and sulphuric acid.

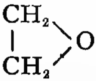
Ethylene Nitrate, $C_2H_4(O.NO_2)_2$, is produced on heating ethylene iodide with silver nitrate in alcoholic solution, or by dissolving glycol in a mixture of concentrated sulphuric and nitric acids:—

$$C_2H_4(OH)_2 + 2NO_2.OH = C_2H_4(O.NO_2)_2 + 2H_2O.$$

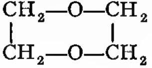
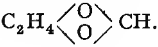
This reaction is characteristic of all hydroxyl compounds (the polyhydric alcohols and polyhydric acids); the hydrogen of hydroxyl is replaced by the NO_2 *group.*

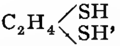
The nitrate is a yellowish liquid, insoluble in water, and has a specific gravity of 1.483 at 8°. It explodes when heated (like the so-called nitroglycerol). The alkalies saponify the esters with formation of nitric acid and glycol.

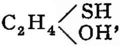
Ethylene Cyanide, $C_2H_4(CN)_2$, is obtained on heating an alcoholic solution of ethylene bromide and potassium cyanide, and in the electrolysis of cyanacetic acid. It forms a crystalline mass, fusing at 54.5°. Boiled with acids or alkalies, it passes into succinic acid, hence may be looked upon as the nitrile of the latter. Nascent hydrogen converts it into butylene diamine, $C_4H_8(NH_2)_2$.

Ethylene Oxide, C_2H_4O =  $\begin{array}{l} CH_2 \\ | \\ CH_2 \end{array} \!\!> O$, is isomeric with acetaldehyde, and is produced on distilling ethylene chlorhydrin or ethylene chloracetin with caustic potash. A mobile, pleasantly smelling, ethereal liquid, which boils at 13.5°, and at 0° has a specific gravity equal to 0.898. It is miscible with water, gradually combining with it to form ethylene glycol.

It unites with the acids to form chlorhydrins and glycol esters. It also precipitates metallic hydroxides from solutions of metallic salts (p. 300).

It combines with bromine, forming a crystalline, red *bromide*, $(C_2H_4O)_2Br$, which melts at 65°, and distils at 95°. Mercury changes the bromide to *diethylene oxide*, $(C_2H_4O)_2$ =  $\begin{array}{ccc} CH_2\text{—}O\text{—}CH_2 \\ | \qquad\quad | \\ CH_2\text{—}O\text{—}CH_2 \end{array}$. This melts at 9°, and distils at 102°. It combines with acetaldehyde to form *ethylene-ethylidene ether*,  $C_2H_4\!\!<\!\!\begin{array}{c}O\\O\end{array}\!\!>\!\!CH.CH_3$, which boils at 82.5°.

Ethylene Thiohydrate,  $C_2H_4\!\!<\!\!\begin{array}{l}SH\\SH\end{array}$, glycol mercaptan, is formed on heating an alcoholic solution of potassium sulphydrate with ethylene bromide (*Berichte*, 19, 3263 and 20, 461). The odor of this compound is something like that of mercaptan. It boils at 146°; its specific gravity is 1.12. Insoluble in water, it dissolves in alcohol and ether. Acids reprecipitate it from alkaline solutions. It throws out mercaptides, *e. g.*, $C_2H_4.S_2Pb$, from the salts of the heavy metals. It yields mercaptals with aldehydes (p. 306). Sodium ethylate and alkyl iodides convert it into dithio-ether, $C_2H_4(S.R)_2$; the stronger organic acids change it to a dithio-ester, *e, g.*, $C_2H_4(S.C_2H_3O)_2$.

The **monothiohydrate**,  $C_2H_4\!\!<\!\!\begin{array}{l}SH\\OH\end{array}$, is obtained when ethylene chlorhydrin acts on potassium sulphydrate. It yields mercaptides with 1 equivalent of the metals.

Ethylene Sulphide, C_2H_4S—isomeric with thioaldehyde, $CH_3.CHS$,—is formed on heating ethylene bromide with alcoholic sodium sulphide. It is only known in its polymeric forms. At first a polymeric ethylene sulphide, $(C_2H_4S)_n$, is formed. This is a white, amorphous powder, insoluble in the ordinary solvents. It melts at 145°, but is not very volatile. Protracted boiling with phenol, changes it to *diethylene disulphide*,  $C_2H_4\!\!<\!\!\begin{array}{c}S\\S\end{array}\!\!>\!\!C_2H_4$. It is analogous to thiophene, and contains a closed chain of six members (*Annalen*, 240, 303). It is similar to naphthalene. It melts at 110°, and boils at 200°. Diethylene sulphide may be synthetically prepared from ethylene mercaptan, $C_2H_4(SH)_2$, by the action of sodium ethylate upon ethylene bromide, and this procedure will also yield the polymeric derivative, if it is desired (*Berichte*, 19, 3263). Another polymeric ethylene sulphide $(C_2H_4S)_n$ (this does not break up) is obtained from ethylene bromide on boiling with aqueous potassium sulphide. It is very similar to the first, but is not decomposed on boiling with phenol. Bromine and diethylene disulphide yield the tetrabromide $(C_2H_4S)_2Br_4$, which silver oxide converts into the oxide $(C_2H_4S_2O)_2$. Nitric acid oxidizes the disulphide into the disulphone $(C_2H_4SO_2)_2$ (p. 307). Methyl iodide and diethylene disulphide unite to the sulphiniodide $(C_2H_4S)_2CH_3I$.

Methyl Sulphurane, $\begin{array}{l}CH_2.S.CH_8\\ |\\ CH_2.S.CH_3\end{array}$, is produced on distilling this iodide with sodium hydroxide. The closed ring of diethylene disulphide is broken.

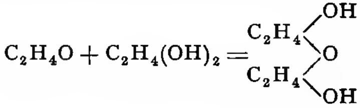
The union of the derivatives of diethylene disulphide with the higher alkyl iodides yields homologous compounds known as **sulphuranes.** They are the alkyl vinyl ethers of thioethylene. Ethyl sulphurane or ethylvinyl ether has been synthetically prepared from glycolchlorhydrin (*Berichte*, 20, 1830; *Annalen*, 240, 305).

The mercaptals are closely related to diethylene disulphide. This is especially true of ethidine dithioethylene, in which there is a closed ring of five members.

Diethylene Tetrasulphide, $C_2H_4\langle{S_2 \atop S_2}\rangle C_2H_4$, is produced by the action of the halogens upon ethylene thiohydrate (or sulphuryl chloride or hydroxylamine, (p. 141). It is a white, amorphous powder, melting about 150° (*Berichte*, 21, 1470).

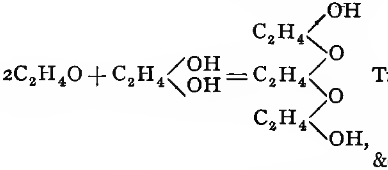
Polyethylene Glycols or *Alcohols.*

The glycols, like the other dihydroxyl compounds (see disulphuric acid), can condense to polyglycols by the coalescence of several molecules, water separating at the same time. These condensed forms arise by the direct union of the glycols with alkylen oxides, especially when heat of 100° is applied:—



$$C_2H_4O + C_2H_4(OH)_2 = \begin{array}{l}C_2H_4\langle{OH \atop }\\ \quad\;\; \rangle O\\ C_2H_4\langle{ \atop OH}\end{array}$$

Diethylene glycol.



$$2C_2H_4O + C_2H_4\langle{OH \atop OH} = \begin{array}{l}C_2H_4\langle{OH \atop }\\ \quad\;\; \rangle O\\ C_2H_4\langle\\ \quad\;\; \rangle O\\ C_2H_4\langle{ \atop OH,}\end{array}$$

Triethylene glycol.

&c.

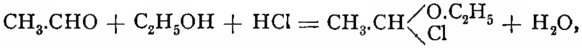
The polyglycols are thick liquids, with high boiling points. They behave like the glycols. Anhydro-acids may be obtained from them by oxidation with dilute nitric acid; thus diglycollic acid (see this) is formed from diethylene alcohol.

Diethylene Glycol, $(C_2H_4)_2O(OH)_2$, boils at 250°. **Triethylene Glycol,** $(C_2H_4)_3O_2(OH)_2$, boils at 285–290°. **Tetraethylene Glycol** boils above 300°.

Ethidene or Ethylidene Compounds.

Ethidene Oxide, $CH_3.CHO$, is ordinary acetaldehyde. On mixing with water heat is evolved, and we may suppose that, perhaps at the time, ethidene dihydrate, $CH_3.CH(OH)_2$, is produced (p. 297). The ether derivatives, the *acetals*, on the contrary, are very stable.

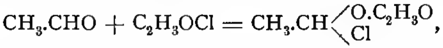
The *alcohol ethers* of ethylidene are formed in the oxidation of alcohols, whereby aldehydes are first produced, and in turn combine with two molecules of the alcohols to yield acetals (p. 300). Hydrochloric acid acting on a mixture of an aldehyde and an alcohol, also produces them, chlorhydrins, however, being the first products:—



$$CH_3.CHO + C_2H_5OH + HCl = CH_3.CH\Big\langle\begin{matrix}O.C_2H_5\\Cl\end{matrix} + H_2O,$$

and from these, through the action of sodium alcoholates, mixed acetals, *e.g.*, methyl butyl acetal, can be obtained (*Berichte*, 19, 3007; see, however, *Berichte*, 17, Ref. 464). On heating the acetals with alcohols, the higher alkyls are displaced by the lower alkyls (*Annalen*, 218, 44). On shaking or digesting the acetals with hydrochloric acid, they are readily resolved into their components and reduce an ammoniacal silver solution with the production of a silver mirror.

The acid chlorides form chlorhydrins:—



$$CH_3.CHO + C_2H_3OCl = CH_3.CH\Big\langle\begin{matrix}O.C_2H_3O\\Cl\end{matrix},$$

from which *mixed* acid acetals can be made by the action of organic silver salts (*Berichte*, 17, 473).

Ethidene-dimethyl Ether, $CH_3.CH\Big\langle\begin{matrix}O.CH_3\\O.CH_3\end{matrix}$, **Dimethyl Acetal,** occurs in crude wood-spirit, and is produced in the oxidation of a mixture of methyl and ethyl alcohols; also upon heating acetaldehyde with methyl alcohol. An ethereal liquid, boiling at 64°; its specific gravity, equals 0.867 at 1°.

Ethidene-methyl-ethyl Ether, $CH_3.CH\Big\langle\begin{matrix}O.C_2H_5\\O.CH_3\end{matrix}$, is produced together with the dimethyl ether in the oxidation of wood-spirit and alcohol. It boils at 80–85°. It is a mixture of dimethyl and diethyl acetal (see above).

Ethidene-diethyl Ether, $CH_3.CH\Big\langle\begin{matrix}O.C_2H_5\\O.C_2H_5\end{matrix}$, **Acetal,** occurs in the course of the distillation of crude spirit and is produced:—

1. By oxidizing alcohol with MnO_2 and sulphuric acid.
2. By heating alcohol and acetaldehyde to 100°.
3. By the action of sodium ethylate upon ethidene bromide and monochlorether.

Acetal is sparingly soluble in water, has an odor somewhat like that of alcohol, and boils at 104°; at 20° its specific gravity equals 0.8314. It is rather stable in presence of alkalies; dilute acids, however, easily convert it into aldehyde and alcohol (*Berichte*, 16, 512). Chlorine produces substitution products; mono-, di-, and tri-chloracetal, $CCl_3.CH.(O.C_2H_5)_2$. Sulphuric acid breaks these up into alcohol and aldehyde (p. 195). *Monochlor-acetal*, $CH_3.CCl(O.C_2H_5)_2$, is most readily obtained by boiling the dichlor-ether with absolute alcohol (*Berichte* 21, 617). It boils at 157°. When heated with alcoholic ammonia, it passes into *acetalamine*, $CH_3.C(NH_2)(O.C_2H_5)_2$, an alkaline liquid, boiling at 163°. It yields condensation products quite readily (*Berichte*, 21, 1482; 22, 568).

Acid esters of ethidene may be prepared by heating ethidene chloride with salts of the fatty acids, and by the union of aldehyde with acids, acid chlorides, and acid anhydrides (p. 248).

Acid chlorides convert ethidene into chlorhydrin:—

$$CH_3.CHO + C_2H_3OCl = CH_3.CH\left\langle\begin{matrix}O.C_2H_3O\\Cl\end{matrix}\right..$$

Mixed acid acetals are obtained from the latter by the action of organic silver salts (*Berichte*, 17, Ref. 473).

Ethidene Chloracetate, $CH_3.CH\left\langle\begin{matrix}O.C_2H_3O\\Cl\end{matrix}\right.$, chlorinated acetic ethyl ester, boils at 121.5°, and is gradually decomposed by water into aldehyde, acetic acid and HCl.

Ethidene Diacetate, $CH_3.CH\left\langle\begin{matrix}O.C_2H_3O\\O.C_2H_3O\end{matrix}\right.$, is not very soluble in water, boils at 188.4°, and is split into aldehyde and acetic acid when boiled with water.

Ethidene Acetpropinate, $CH_3.CH\left\langle\begin{matrix}O.C_2H_3O\\O.C_2H_3O\end{matrix}\right.$, boiling at 178.6°, is identical with ethidene propio-acetate (see above). *This is a further proof of the equivalence of the carbon affinities* (*Annalen*, 225, 267).

Aldehyde ammonia, $CH_3.CH\left\langle\begin{matrix}NH_2\\OH\end{matrix}\right.$, and aldehyde hydrocyanide (oxycyanide), $CH_3.CH\left\langle\begin{matrix}CN\\OH\end{matrix}\right.$ (p. 190), are also ethidene compounds.

SULPHUR COMPOUNDS.

The thio-acetals are perfectly similar to the acetals. They have been called mercaptals and mercaptols. Mercaptals are formed from mercaptans and aldehydes by the interaction of HCl:—$CH_3.CHO + 2C_2H_5SH = CH_3.CH\left\langle\begin{matrix}S.C_2H_5\\S.C_2H_5\end{matrix}\right. + H_2O$. The mercaptols are obtained in the same manner from the ketones, *e.g.*, $(CH_3)_2CO$. These thio-acetals are insoluble in water and generally liquid compounds. They are quite stable and are not changed by boiling with alkalies or acids (*Berichte*, 18, 883; 19, 2803). Analogous compounds are obtained with the ketonic acids (*Berichte*, 19, 1787).

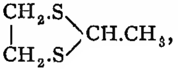
Instead of using the mercaptans for the preparation of the mercaptols, employ the alkyl-thiosulphates. Hydrochloric acid decomposes these into primary sulphates and mercaptans, and the latter, in the presence of acetones, immediately yield the mercaptols (*Berichte*, 22, Ref. 115).

Methylene Mercaptal, $CH_2(S.C_2H_5)_2$, has been obtained from methylene iodide by the action of sodium ethyl mercaptide. It is an oil, boiling at 180°.

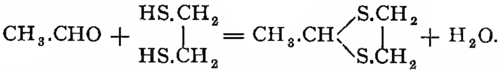
Ethidene Dithioethyl, $CH_3.CH(S.C_2H_5)_2$, dithioacetal, the ethyl mercaptal of acetaldehyde, is a very mobile liquid, with an odor like that of thioaldehyde. It is lighter than water and boils at 186°.

Acetone Dithioethyl, $(CH_3)_2C(S.C_2H_5)_2$, the ethyl mercaptal of acetone, boils at 190° (*Berichte*, 19, 1787; 22, 2595). Permanganate of potassium oxidizes it to **sulphonal.**

Propidene-dithio ethyl, $C_2H_5.CH(S.C_2H_5)_2$, from propionic aldehyde and ethyl mercaptan, boils about 198°.

Ethylene Mercaptals, *e.g.*, 
$\begin{matrix}CH_2.S\\|\\CH_2.S\end{matrix}\!\!>CH.CH_3$, and **Ethylene Mercaptols,**

are similarly produced by the action of ethylene mercaptan upon aldehydes and ketones (*Berichte*, 21, 1473):—



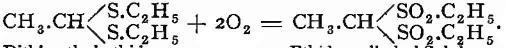
$$CH_3.CHO + \begin{array}{l}HS.CH_2\\ \;|\\ HS.CH_2\end{array} = CH_3.CH\left<\begin{array}{l}S.CH_2\\ \;|\\ S.CH_2\end{array}\right. + H_2O.$$

They contain a nucleus of five members. It is somewhat less stable than the nucleus of diethylene disulphide, containing six members (p. 304).

Ethylene-dithio-ethidene, $C_2H_4S_2:CH.CH_3$. An oil boiling at 173°.

DISULPHONES.

These are produced in oxidizing the dithio-ethers or thioacetals with a permanganate solution. Each sulphur atom takes up two oxygen atoms:—



$$CH_3.CH\left<\begin{array}{l}S.C_2H_5\\ S.C_2H_5\end{array}\right. + 2O_2 = CH_3.CH\left<\begin{array}{l}SO_2.C_2H_5\\ SO_2.C_2H_5\end{array}\right..$$

Dithio-ethyl-ethidene. Ethidene-diethyl Sulphone.

Mercaptals yield disulphones of the type $RCH(SO_2.C_2H_5)_2$, and the mercaptols those of the form $R_2C(SO_2.C_2H_5)_2$. A third class of disulphones is known: $CH_2(SO_2.C_2H_5)_2$, obtained by oxidizing ortho-thio-formic ester, $CH(S.C_2H_5)_3$.

In the disulphones of the first and third classes the hydrogen of the groups CH_2 and CRH can be easily replaced by the halogens, and by the alkali metals (*Berichte*, 21, 652). This is similar to the substitutions in aceto-acetic ester and malonic ester. The alkali metals which enter can be further replaced by alkyls (*Berichte*, 21, 185; 22, Ref. 678):—

$$CH_3.CH(SO_2.C_2H_5)_2 \text{ yields } \begin{array}{l}CH_3\\ CH_3\end{array}\!\!>C(SO_2.C_2H_5)_2.$$

Ethidene-diethyl Sulphone. Acetone-diethyl Sulphone.

These disulphones are solid, crystalline and very stable compounds. Acids and alkalies do not attack them.

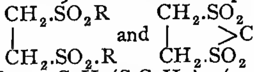
Methylene-diethylsulphone, $CH_2(SO_2.C_2H_5)_2$, is formed by the oxidation of trithioformic ester and methylene mercaptal. It crystallizes in needles, melting at 104°. It is very soluble in alcohol and water.

Ethidene-diethylsulphone, $CH_3.CH(SO_2.C_2H_5)_2$, from ethidene mercaptal, has also been prepared from α-dithio-ethylpropionic acid. It melts at 75° and boils at 320° without decomposition.

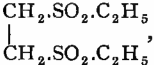
Acetone-diethylsulphone, $(CH_3)_2C(SO_2.C_2H_5)_2$, **Sulphonal,** is made by oxidizing acetone-ethyl-mercaptol with permanganate. It also results from the action of sodium hydroxide and methyl iodide (*Annalen*, 253, 147) upon ethidene-diethylsulphone. It dissolves in 100 parts water at 16°, in 20 parts at 100°, and readily in alcohol.

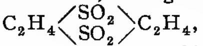
It crystallizes in colorless leaflets or plates, melting at 126°. It is odorless and tasteless. In doses of 0.5–3 gr. it is used as a hypnotic.

Consult *Berichte*, 22, 678 and 829 for additional sulphones.



Ethylene Disulphones, $\begin{array}{l}CH_2.SO_2R\\ \;|\\ CH_2.SO_2.R\end{array}$ and $\begin{array}{l}CH_2.SO_2\\ \;|\\ CH_2.SO_2\end{array}\!\!>CH.R$, result from the oxidation of ethylene dithio-ethers, $C_2H_4(S.C_2H_5)_2$ (p. 303), and ethylene-mercaptals and mercaptols (p. 306). These sulphones are saponified and decomposed on boiling with alkalies (*Berichte*, 21, 1474).

Ethylene-diethylsulphone,  $\begin{array}{l}CH_2.SO_2.C_2H_5\\ |\\ CH_2.SO_2.C_2H_5\end{array}$, has been obtained from ethylene bromide by the action of 2 molecules of sodium ethyl sulphinate, and from sodium ethylene disulphinate (p. 303) by the action of 2 molecules of ethyl bromide. The hexavalence of sulphur in the sulphones is thus proved (see p. 144 and *Berichte*, 21, Ref. 102). It yields colorless needles, melting at 137°.

Diethylene Disulphone,  $C_2H_4\begin{array}{c}\diagup SO_2 \diagdown\\ \diagdown SO_2 \diagup\end{array}C_2H_4$, results from the oxidation of diethylenedisulphide (p. 303), and ethylene disulphinate of sodium with ethylene bromide.

Trimethylene trisulphone (p. 193), trialdehyde trisulphones (p. 197), and triacetone trisulphone (p. 205) are examples of trisulphones.

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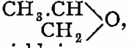
2. Propylene Glycols, $C_3H_8O_2 = C_3H_6(OH)_2$.

The two glycols theoretically possible are known :—

$$\underset{\alpha\text{-Propylene Glycol.}}{CH_3.CH(OH).CH_2.OH} \text{ and } \underset{\beta\text{-Propylene Glycol.}}{CH_2(OH).CH_2.CH_2.OH}.$$

α-Propylene Glycol is obtained by heating propylene bromide with silver acetate and saponifying the acetic ester first produced with caustic potash. Propylene chloride heated with water and lead oxide also yields it. It is most readily prepared by distilling glycerol with sodium hydroxide (*Berichte*, 13, 1805). It is a thick liquid, with sweetish taste. It boils at 188°. At 0° its specific gravity equals 1.051. Platinum black oxidizes it to ordinary lactic acid. Only acetic acid is formed when chromic acid is the oxidizing agent. Concentrated hydriodic acid changes it to isopropyl alcohol and its iodide.

When exposed to the action of the ferment *Bacterium termo*, ordinary propylene glycol becomes optically active and yields an active propylene oxide (*Berichte*, 14, 843).

Propylene Diacetate, $C_3H_6(O.C_2H_3O)_2$, boils at 186°; specific gravity 1.109 at 0°. The *α-chlorhydrin*, $CH_3.CH(OH).CH_2Cl$, is produced when sulphuric acid and water act upon allyl chloride. It boils at 127° and is oxidized to mono-chloracetic acid by nitric acid. *β-Chlorhydrin*, $CH_3.CHCl.CH_2.OH$, is produced by adding ClOH to propylene. This also boils at 127°, but on oxidation yields α-chlorpropionic acid, $CH_3.CHCl.CO.OH$. *α-Propylene Oxide*,  $\begin{array}{l}CH_3.CH\diagdown\\ \quad\;\; CH_2\diagup\end{array}O$, from the chlorhydrins, boils at 35°, is readily soluble in water, and yields isopropyl alcohol, $CH_3.CH(OH).CH_3$, with nascent hydrogen.

β-Propylene Glycol, $CH_2(OH).CH_2.CH_2(OH)$, trimethylene glycol, is formed by boiling trimethylene bromide with a large quantity of water or potassium carbonate (*Berichte*, 16, 393). Its formation from glycerol in the *schizomycetes-fermentation* is worthy of note. It is a thick liquid, miscible with water and alcohol, boiling at 216°, and having a specific gravity at 0° of 1.065. Hydrobromic acid changes it to bromhydrin, which yields γ-oxybutyric acid with potassium cyanide. Moderately oxidized it forms β-oxypropionic acid.

Its *diacetate*, $CH_2(CH_2.O.C_2H_3O)_2$, boils at 210°; its specific gravity at 19° is 1.07. The chlorhydrin, $CH_2Cl.CH_2.CH_2.OH$, is obtained by conducting HCl into glycol. It boils at 160°, and its specific gravity at 0° is 1.146. It is soluble in 2 volumes of water, and, when oxidized with chromic acid, becomes β-chlorpropionic acid. *Trimethylene oxide*,  $CH_2\left\langle\begin{matrix}CH_2\\CH_2\end{matrix}\right\rangle O$, is prepared by heating chlorhydrin with caustic potash. A mobile liquid, with penetrating odor, and boiling at 50°. It mixes readily with water and condenses without difficulty.

3. Butylene Glycols, $C_4H_{10}O_2 = C_4H_8(OH)_2$.

Four of the six possible butylene glycols (p. 298) are known.

(1) α-**Butylene Glycol**, $CH_3.CH_2.CH(OH).CH_2.OH$, is obtained from α-butylene bromide; boils at 191–192°, and at 0° has a specific gravity of 1.0189. Nitric acid oxidizes it to glycollic and glyoxylic acids.

(2) β-**Butylene Glycol**, $CH_3.CH(OH).CH_2.CH_2.OH$, is formed in slight quantity, together with ethyl alcohol, in the action of sodium amalgam upon aqueous acetaldehyde (p. 193). Aldol very probably appears as an intermediate product in this reaction, and from it the glycol can be directly made by the use of sodium amalgam (*Berichte*, **16**, 2505):—

$$CH_3.CH(OH).CH_2.CHO + H_2 = CH_3.CH(OH).CH_2.CH_2.OH.$$

β-Butylene glycol is a thick liquid, which boils at 207°, and mixes with both water and alcohol. When oxidized by either nitric or chromic acid it forms acetic and oxalic acids (along with some crotonaldehyde).

Aldol is the aldehyde of butylene glycol.

(3) γ-**Butylene Glycol**, $CH_3.CH(OH).CH(OH).CH_3$, is formed from β-butylene bromide. It boils at 183–184°. Its specific gravity at 0° equals 1.048. Nitric acid oxidizes it to oxalic acid.

(4) **Isobutylene Glycol**, $(CH_3)_2.C(OH).CH_2.OH$, is obtained from isobutylene bromide. It boils at 176–178°. At 0° its specific gravity is 1.0129. Nitric acid converts it into α-oxyisobutyric acid.

Its *chlorhydrin*, $(CH_3)_2:CCl.CH_2.OH$, is produced by adding ClOH to isobutylene. It boils at 128–130°, and when oxidized becomes chlor-isobutyric acid.

(5) **Tetramethylene Glycol**, $CH_2(OH).(CH_2)_2.CH_2.OH$, has been obtained from tetramethylene-diamine (p. 313). Its dibromide boils at 190°.

4. **Amylene Glycols**, $C_5H_{12}O_2 = C_5H_{10}(OH)_2$.

(1) β-**Amylene Glycol**, $CH_3.CH_2.CH(OH).CH(OH).CH_3$, is derived from

β-amylene bromide (p. 84). It boils at 187°. Its specific gravity at 0° is 0.994. By oxidation it yields α-oxybutyric acid and acetic acid.

(2) **α-Isoamylene Glycol,** $(CH_3)_2CH.CH(OH).CH_2(OH)$, from α-isoamylene bromide, boils at 206°. Its specific gravity at 0° is 0.998. When oxidized it yields oxy-isovaleric acid.

(3) **β-Isoamylene Glycol,** $(CH_3)_2C(OH).CH(OH).CH_3$, from β-isoamylene bromide, boils at 177°. Its specific gravity at 0° is 0.967. When oxidized it yields α-oxy-isobutyric acid.

(4) **γ-Pentylene Glycol,** $CH_3.CH(OH).CH_2.CH_2.CH_2.OH$, is formed from aceto-propyl alcohol, $CH_3.CO.CH_2.CH_2.CH_2.OH$ (p. 322), by the action of sodium amalgam. A thick oil, very soluble in water, and boiling at 219°. At this temperature it partly decomposes into water and γ-pentylene oxide, $C_5H_{10}O$, boiling about 80°. The latter product is tetrahydromethylfurfurane, C_4H_7O (*Berichte*, 22, 2567).

(5) **Pentamethylene Glycol,** $CH_2\begin{matrix}\diagup CH_2.CH_2.OH \\ \diagdown CH_2.CH_2.OH\end{matrix}$, obtained by the action of silver nitrite upon pentamethylene-diamine hydrochloride (p. 313), boils at 260°.

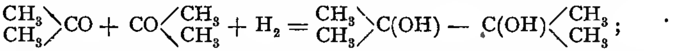
5. **Hexylene Glycols,** $C_6H_{14}O_2$.

(1) **Hexylene Glycol,** $C_6H_{12}(OH)_2$, from hexylene bromide, boils at 207°. Its specific gravity at 0° is 0.967.

(2) **Diallyl Hydrate,** $C_6H_{12}(OH)_2$, is obtained from diallyl, $(C_3H_5)_2$ (p. 89), by means of the HI-compound, $C_6H_{12}I_2$. It boils at 212–215°.

(3) **δ-Hexylene Glycol,** $CH_3.CH(OH).(CH_2)_3.CH_2OH$, is obtained from aceto-butyl alcohol, $CH_3.CO.C_4H_9.OH$ (p. 322), by the action of sodium amalgam. It boils near 235° (under 710 mm. pressure) and speedily passes into *δ-hexylene oxide*, $C_6H_{12}O$, boiling at 105° C. (p. 300).

(4) **Tetramethyl-ethylene Glycol,** $(CH_3)_2.C(OH).C(OH.(CH_3)_2$, or **Pinacone,** is formed, together with isopropyl alcohol, when sodium amalgam or sodium acts upon aqueous acetone (p. 203).



$$\begin{matrix}CH_3 \diagdown \\ CH_3 \diagup\end{matrix}CO + CO\begin{matrix}\diagup CH_3 \\ \diagdown CH_3\end{matrix} + H_2 = \begin{matrix}CH_3 \diagdown \\ CH_3 \diagup\end{matrix}C(OH) - C(OH)\begin{matrix}\diagup CH_3 \\ \diagdown CH_3\end{matrix};$$

it can be obtained, too, from the bromide of tetramethyl-ethylene (from dimethyl-isopropyl-carbinol). It crystallizes from its aqueous solution in the form of the hydrate, $C_6H_{14}O_2 + 6H_2O$, which consists of large quadratic plates, melting at 42°, and gradually efflorescing on exposure. In the anhydrous state it is a crystalline mass which melts at 38° and boils at 171–172°.

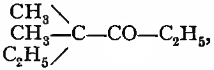
When heated with dilute sulphuric or hydrochloric acid pinacone parts with 1 molecule of water, and by molecular transposition, becomes *pinacoline*, $C_6H_{12}O$ (p. 203).

Dimethyl-pinacone is the representative of a series of similarly constituted glycols—the **pinacones.** These contain two hydroxyl groups attached to two adjoining carbon atoms, which in turn are linked to two alkyls. All the pinacones show similar deportment, in that when they are heated with acids they part with water and suffer molecular transposition into ketones—the pinacolines (p. 202)—see also benzpinacone.

Another pinacone of the fatty series is :—

Methyl-ethyl Pinacone, $\begin{matrix}CH_3 \diagdown \\ C_2H_5 \diagup\end{matrix}C(OH).C(OH)\begin{matrix}\diagup CH_3 \\ \diagdown C_2H_6\end{matrix}$. This is obtained from $\begin{matrix}CH_3 \diagdown \\ C_2H_5 \diagup\end{matrix}CO$. It is a crystalline mass, melting at 28°, and boiling at 200–

205°. It does not form a hydrate with water. When heated with sulphuric acid (diluted with 1 part water) it yields pinacoline by a transposition of the methyl group:—



$$\begin{matrix}CH_3\diagdown & \\ CH_3—C—CO—C_2H_5, \\ C_2H_5\diagup & \end{matrix}$$

Ethyl-tertiary-amyl-ketone.

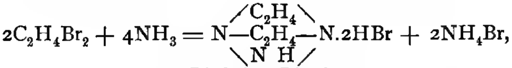
This is a liquid with an odor like that of camphor, and boils at 145–150°. When oxidized with chromic acid it decomposes into acetic acid and dimethylethyl acetic acid, $\begin{matrix}(CH_3)_2\\C_2H_5\end{matrix}\!\!>C.CO_2H$.

The higher glycols have received very little attention.

AMINES OF THE DIVALENT RADICALS.

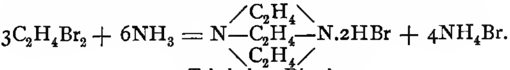
The di-, like the mono-valent alkyls, can replace two hydrogen atoms in two ammonia molecules and produce primary, secondary, and tertiary *diamines*. These are di-acid bases, and are capable of forming salts by direct union with two equivalents of acids. They are prepared by heating the alkylen bromides with alcoholic ammonia to 100° (p. 157) in sealed tubes:—

$$\underset{\text{Ethylene Bromide.}}{C_2H_4Br_2} + 2NH_3 = \underset{\text{Ethylene Diamine.}}{C_2H_4{<}\begin{matrix}NH_2\\NH_2\end{matrix}.2HBr},$$



$$2C_2H_4Br_2 + 4NH_3 = N\begin{matrix}\diagup C_2H_4 \diagdown\\ —C_2H_4— \\ \diagdown N\ H \diagup\end{matrix}N.2HBr + 2NH_4Br,$$

Diethylene Diamine.



$$3C_2H_4Br_2 + 6NH_3 = N\begin{matrix}\diagup C_2H_4 \diagdown\\ —C_2H_4— \\ \diagdown C_2H_4 \diagup\end{matrix}N.2HBr + 4NH_4Br.$$

Triethylene Diamine.

To liberate the diamines, the mixture of their HBr-salts is distilled with KOH and the product then fractionated.

Another very convenient method for the preparation of diamines is the reduction of alkylen dicyanides (p. 313) with metallic sodium and absolute alcohol (see p. 159 and *Berichte*, 20, 2215):—

$$\underset{\text{Ethylene Cyanide.}}{\begin{matrix}CH_2.CN\\|\\CH_2.CN\end{matrix}} + 4H_2 = \underset{\text{Tetramethylene Diamine.}}{\begin{matrix}CH_2.CH_2.NH_2\\|\\CH_2.CH_2.NH_2\end{matrix}}.$$

In the primary and secondary diamines the amid-hydrogen (by action of alkyl iodides) can be further substituted by alkyls, whereas the tertiary diamines unite with the alkyl iodides to ammonium iodides.

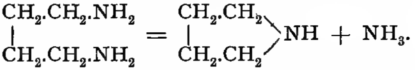
Further, the diamines unite directly with water, forming *ammonium oxides*:—

$$C_2H_4{<}\begin{matrix}NH_2\\NH_2\end{matrix} + H_2O = C_2H_4{<}\begin{matrix}NH_3\\NH_3\end{matrix}{>}O.$$

These compounds are very stable, and only lose water when distilled over KOH. They part with water when acted upon with acids and yield diamine salts.

Acid derivatives result from the action of acid chlorides upon the diamines. The formation of the dibenzoyl compounds, *e. g.*, $C_2H_4(NH.CO.C_6H_5)_2$, on shaking benzoyl chloride and sodium hydroxide with the diamines, is employed for the detection of the latter (*Berichte*, 21, 2744).

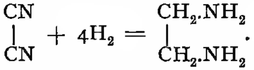
The separation of ammonia from the diamines gives rise to the *imines*, which may be compared to the acid-imides. They also appear together with the diamines in the reduction of the alkylen cyanides (see above), and are directly obtained from the diamines upon heating their HCl-salts (*Berichte*, 18, 2956):—



These *imines* are identical with the tetrahydro-compounds of the pyrrol and pyridine bases.

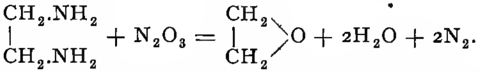
Of the many diamine derivatives formed by these methods, we may cite the following:—

Ethylene Diamine, $C_2H_4{<}\genfrac{}{}{0pt}{}{NH_2}{NH_2}$, is a colorless liquid, boiling at 123°. It reacts strongly alkaline, and has an ammoniacal odor. It is also produced when nascent hydrogen (tin and HCl) acts upon dicyanogen (p. 265):—



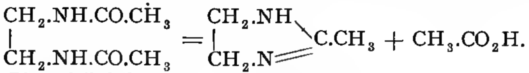
$$\begin{matrix}CN\\|\\CN\end{matrix} + 4H_2 = \begin{matrix}CH_2.NH_2\\|\\CH_2.NH_2\end{matrix}.$$

Nitrous acid converts it into ethylene oxide, ethylene glycol being very probably first formed (p. 161):—



Ethylene diamine, like the ortho-diamines of the benzene series, combines with ortho-diketones, *e.g.*, phenanthraquinone and benzil, to form tetrahydropyrazin-derivatives (*Berichte*, 20, 267). It also unites with the benzaldehydes and benzoketones (*Berichte*, 20, 276; 21, 2358).

Diacetyl-diethylene Diamine, $C_2H_4(NH.C_2H_3O)_2$, is produced by the action of acetic anhydride upon ethylene diamine. It consists of colorless needles, melting at 172°. When this compound is heated beyond its melting point, water splits off, and there follows an inner condensation that leads to the formation of an *amidine base* (p. 293) (*Berichte*, 21, 2332):—

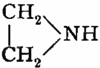


Diacetyl-diethylene Diamine. Ethylene-ethenyl Amidine.

The derivatives of other acids, as well as the propylene diamine and trimethylene derivatives, react similarly. These amidine bases are intimately related to the glyoxalines.

Ethylene-ethenyl Amidine, $C_2H_4{:}N_2H{:}C_2H_3$, or **Ethylene acetamidine**, is a white crystalline mass very readily soluble in water. It melts at 88°, and boils about 223°.

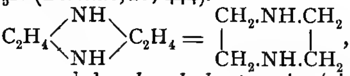
On heating its HCl-salt, a molecule of NH_3 escapes from ethylene diamine, and there results *ethylene imine*,



$\left.\begin{array}{l} CH_2 \\ | \\ CH_2 \end{array}\right\rangle NH$

(see above), which is apparently identical with the base *spermine*, C_2H_5N (*Berichte*, 20, 444).

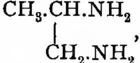
Di-ethylene Diamine,



$C_2H_4\left\langle\begin{array}{c} NH \\ NH \end{array}\right\rangle C_2H_4 = \begin{array}{l} CH_2.NH.CH_2 \\ | \qquad\quad\ | \\ CH_2.NH.CH_2 \end{array}$

, containing a chain of six members, is to be regarded as *hexahydro-pyrazine* (piperazine). It is formed in the action of ethylene bromide on ethylene diamine. It is a liquid, boiling at 172° (*Berichte*, 20, 444).

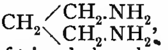
Propylene Diamine,



$\begin{array}{l} CH_3.CH.NH_2 \\ \quad\ | \\ \quad CH_2.NH_2 \end{array}$

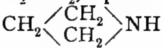
, from propylene bromide and alcoholic ammonia, is a liquid, boiling at 117°–120°. Its diacetyl derivative yields an amidine base when heated.

Trimethylene Diamine,



$CH_2\left\langle\begin{array}{l} CH_2.NH_2 \\ CH_2.NH_2 \end{array}\right.$

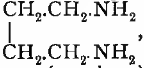
, from trimethylene bromide, boils at 135°–136°. By the action of trimethylene bromide upon potassium phthalimide, a derivative of γ-brompropylamine, $CH_2Br.CH_2.CH_2.NH_2$, is produced. This loses water, and apparently yields *trimethylene-imine*,



$CH_2\left\langle\begin{array}{c} CH_2 \\ CH_2 \end{array}\right\rangle NH$

(*Berichte*, 21, 2678).

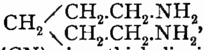
Tetramethylene Diamine, $C_4H_8(NH_2)_2 =$



$\begin{array}{l} CH_2.CH_2.NH_2 \\ | \\ CH_2.CH_2.NH_2 \end{array}$

, is obtained from ethylene cyanide by the action of nascent hydrogen (see above), and by the action of hydroxylamine upon pyrrol, C_4H_4NH, accompanied by further reduction (*Berichte*, 22, 1968). It is identical with the *putrescine* (*Berichte*, 21, 2938), which has been isolated from decaying matter. It is a liquid with a peculiar odor. It fumes in the air, and boils at 156°–160° It solidifies on cooling to a crystalline mass, melting at 24°. There is always present with the diamine a slight quantity of *tetramethylen-imine*, $C_4H_8{:}NH$ (see above), which can be directly obtained by heating the HCl-salt of the diamine. It is identical with pyrrolidine or tetrahydropyrrol.

Pentamethylene Diamine, $C_5H_{10}(NH_2)_2 =$

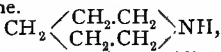


$CH_2\left\langle\begin{array}{l} CH_2.CH_2.NH_2 \\ CH_2.CH_2.NH_2 \end{array}\right.$

, obtained by the reduction of trimethylene cyanide, $C_3H_6(CN)_2$, is a thick liquid, with an odor resembling that of piperidine. It boils at 178°–179°, and solidifies in the cold. Its specific gravity at 0° is 0.9174 (*Berichte*, 18, 2956; 19, 780). It is identical with *cadaverine* (p. 316), a ptomaine isolated from decaying corpses (*Berichte*, 20, 2216 and Ref. 69).

Neuridine, $C_5H_{14}N_2$ (*Berichte*, 18, 86), formed by the decay of fish and meat, is isomeric with pentamethylene diamine.

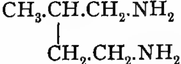
Pentamethylenimine, $C_5H_{11}N =$



$CH_2\left\langle\begin{array}{l} CH_2.CH_2 \\ CH_2.CH_2 \end{array}\right\rangle NH$

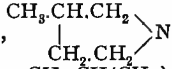
, from trimethylencyanide, and also from its HCl-salt, is identical with piperidine-hexahydropyridine (*Berichte*, 18, 2956).

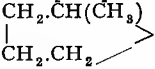
β-Methyl-tetramethylene Diamine,

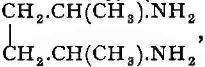


$\begin{array}{l} CH_3.CH.CH_2.NH_2 \\ \quad\ | \\ \quad CH_2.CH_2.NH_2 \end{array}$

, from pyrotartaric acid nitrile, $CH_3.C_2H_3(CN)_2$, boils at 172°–173°, and by splitting off NH_3, yields

β-Methyl Pyrrolidine,  $\left.\begin{array}{l}CH_3.CH.CH_2\\ \quad|\\ CH_2.CH_2\end{array}\right>N$, boiling at 103° (*Berichte*, 20, 1654).

α-Methyl Pyrrolidine,  $\left|\begin{array}{l}CH_2.CH(CH_3)\\ \\ CH_2.CH_2\end{array}\right>NH$, is produced by the reduction of γ-amido valeric acid. It boils at 97° (*Berichte*, 22, 1866).

Diamido Hexane,  $\begin{array}{l}CH_2.CH(CH_3).NH_2\\ |\\ CH_2.CH(CH_3).NH_2\end{array}$, is formed in the reduction of the diphenylhydrazone of acetonyl acetone. It boils at 175°. On splitting off NH_2, it becomes (1.4)-**Dimethyl Pyrrolidine,** boiling at 107° (*Berichte*, 22, 1859).

By permitting the tertiary monamines to act upon ethylene bromide we obtain the bromides of ammonium bases:—

$$(C_2H_5)_3N + C_2H_4Br_2 = \left.\begin{array}{l}(C_2H_5)_3\\ C_2H_4Br\end{array}\right\}\overset{v}{N}.Br.$$

The bromine attached to the nitrogen of these compounds can be readily replaced, whereas, the other bromine atom is more intimately combined. Silver nitrate produces the nitrate of triethyl-bromethyl-ammonium:—

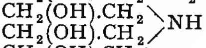
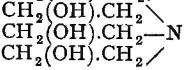
$$\left.\begin{array}{l}(C_2H_5)_3\\ C_2H_4Br\end{array}\right\}N.O.NO_2.$$

And by the action of moist silver oxide, the bromine atom in union with carbon is also attacked, HBr separates, and the group, $CH_2Br.CH_2$, is changed to the vinyl group, $CH_2:CH$. In this manner we get the *triethyl-vinyl-ammonium base*

$$\left.\begin{array}{l}(C_2H_5)_3\\ C_2H_3\end{array}\right\}\overset{v}{N}.OH.$$

OXYETHYL BASES OR HYDRAMINES.

When ethylene oxide and aqueous ammonia act upon each other, 1, 2 and 3 molecules of ethylene oxide unite with 1 molecule of ammonia, and form the bases:—

$CH_2(OH).CH_2.NH_2$	Ethylene Hydramine.
 $\left.\begin{array}{l}CH_2(OH).CH_2\\ CH_2(OH).CH_2\end{array}\right>NH$	Diethylene "
 $\begin{array}{l}CH_2(OH).CH_2\diagdown\\ CH_2(OH).CH_2—N\\ CH_2(OH).CH_2\diagup\end{array}$	Triethylene "

The HCl-salts of these bases are produced by the action of ethylene chlorhydrin, $CH_2Cl.CH_2.OH$, upon ammonia. The bases are separated by fractional crystallization of their HCl-salts, or platinum double salts. They are thick, strongly alkaline liquids, which decompose upon distillation.

The alkylen oxides and their chlorhydrins also combine with the amines. Such oxyalkyl bases may be obtained from the allyl amines by addition of water (by the action of H_2SO_4 (*Berichte*, 16, 532). The bases obtained from the secondary amines are *alkamines* or *alkines* (*Berichte*, 15, 1143):—

$$(C_2H_5)_2NH + CH_2Cl.CH_2.OH = (C_2H_5)_2N.CH_2.CH_2OH + HCl.$$

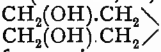
Triethyl Alkamine.

When digested with organic acids and hydrochloric acid, these oxyethyl bases yield (by replacement of the hydrogen of OH by acid radicals) ester-like compounds, termed Alkeïnes (see Tropeïne).

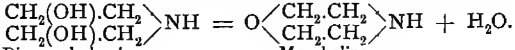
Oxy-ethylamine, $CH_2OH.CH_2\ NH_2$, amido-ethyl alcohol, is produced when vinylamine is evaporated with nitric acid (*Berichte*, 21, 2668).

Oxy-ethylmethylamine, $CH_2OH.CH_2\ NH.CH_3$, results from ethylene chlorhydrin and methylamine when they are exposed to a temperature of 110°. It is a liquid, boiling at 130–140°.

Oxy-ethyldimethylamine, $CH_2OH.CH_2.N(CH_3)_2$, has been obtained in the decomposition of morphine (*Berichte*, 22, 1115). It boils at 128–130°.

Dioxy-ethylamine,  $\begin{matrix}CH_2(OH).CH_2\\CH_2(OH).CH_2\end{matrix}\Big\rangle NH = C_4H_{11}NO_2$, imido-ethyl alcohol, is formed in the action of ammonia upon ethylene oxide and glycol chlorhydrin.

If this compound be heated to 160° with hydrochloric acid and distilled with caustic potash it loses water, and yields an *inner anhydride*, C_4H_9NO:—



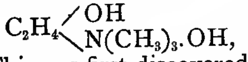
$$\begin{matrix}CH_2(OH).CH_2\\CH_2(OH).CH_2\end{matrix}\Big\rangle NH = O\Big\langle\begin{matrix}CH_2.CH_2\\CH_2.CH_2\end{matrix}\Big\rangle NH + H_2O.$$

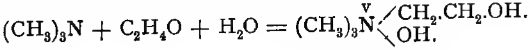
Dioxy-ethylamine. Morpholine.

This contains a closed, six-membered nucleus, consisting of four C-atoms, one O-atom, and one N-atom. It is the tetrahydro-derivative of *Para-azoxine*, C_4H_5NO. It has been called *morpholine*, as it is very probable that an analogous atomic grouping exists in morphine.

Alkylized morpholines, $C_4H_8N(R)O$ (*Berichte*, 22, 2081), are produced in an analogous manner from the dioxy-ethyl alkylamines, $[CH_2(OH).CH_2]_2NR$.

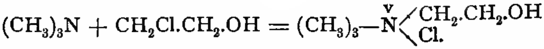
The bases obtained from the tertiary amines are especially interesting. Choline is one of them. It is quite important physiologically.

Choline,  $C_5H_{15}NO_2 = C_2H_4\Big\langle\begin{matrix}OH\\N(CH_3)_3.OH,\end{matrix}$ oxyethyl-trimethyl ammonium hydroxide. This was first discovered in the bile (hence called choline or bilineurine). It is quite widely distributed in the animal organism, especially in the brain, and in the yolk of egg, in which it is present as *lecithin*, a compound of choline with glycero-phosphoric acid and fatty acids. It is present in hops, hence occurs in beer. It is obtained, too, from sinapin (the alkaloid of *Sinapis alba*), when it is boiled with alkalies (hence the name *sincalin*). Choline is artifically prepared by heating trimethylamine with ethylene oxide in aqueous solution:—



$$(CH_3)_3N + C_2H_4O + H_2O = (CH_3)_3\overset{v}{N}\Big\langle\begin{matrix}CH_2.CH_2.OH.\\OH.\end{matrix}$$

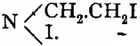
Its hydrochloride is produced by means of ethylene chlorhydrin :—



$$(CH_3)_3N + CH_2Cl.CH_2.OH = (CH_3)_3{-}\overset{v}{N}\begin{matrix}\diagup CH_2.CH_2.OH\\ \diagdown Cl.\end{matrix}$$

Choline deliquesces in the air and crystallizes with difficulty. It possesses a strong alkaline reaction and absorbs CO_2. Its platinum double salt, $(C_5H_{14}ONCl)_2.PtCl_4$, crystallizes in beautiful reddish-yellow plates, insoluble in alcohol.

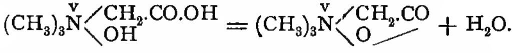
Isocholine, $CH_3.CH(OH).N(CH_3)_3.OH$, isomeric with choline, is obtained by introducing CH_3 into aldehyde-ammonia (*Berichte*, 16, 207). *Muscarine*, $C_2H_3(OH)_2.N(CH_3)_3.OH$, is an oxycholine. It is found in fly agaric, and is formed by oxidizing choline with HNO_3.

When choline is heated with hydriodic acid, we obtain the compound, $(CH_3)_3$  $N\begin{matrix}\diagup CH_2.CH_2I\\ \diagdown I.\end{matrix}$ This moist silver oxide converts into *vinyl-trimethyl-ammonium hydroxide* :—

$$(CH_3)_3\overset{v}{N}\begin{matrix}\diagup CH{:}CH_2\\ \diagdown OH\end{matrix} = C_5H_{13}NO.$$

This base resembles choline; it has also been obtained from the brain substance, and bears the name **Neurine**. It is very poisonous. It is produced when choline decomposes, or upon boiling it with baryta water. It occurs with the *ptomaïnes*—alkaloids of decay, partly poisonous and partly non-toxic. This decomposition is due to pathogenic bacteria, and the first product is choline, then *neuridine*, $C_5H_{14}N_2$ (p. 313), and *trimethylamine*. Later, *cadaverine*, $C_5H_{14}N_2$, identical with pentamethylene diamine (p. 313), *putrescine*, $C_4H_{12}N_2$, identical with tetramethylendiamine, and *saprine*, $C_5H_{14}N_2$, appear, and with them the toxic oxygen bases *mydatoxine*, $C_6H_{13}NO_2$, and *mydine*, $C_8H_{11}NO$. *Mytilotoxine*, $C_6H_{15}NO_2$, has been prepared from a poisonous mussel. It is similar to curara (see Brieger, *Berichte*, 20, Ref. 68, upon ptomaïnes).

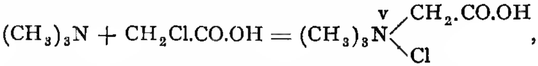
Betaïne (oxyneurine, lycine), $C_5H_{11}NO_2$, is allied to choline. It must be considered as trimethyl glycocoll (see this). It is obtained by the careful oxidation of choline, when the primary alcohol group, $CH_2.OH$, is converted into $CO.OH$, and the ammonium hydroxide that is first formed parts with a molecule of water (see Amido-acids) :—



$$(CH_3)_3\overset{v}{N}\begin{matrix}\diagup CH_2.CO.OH\\ \diagdown OH\end{matrix} = (CH_3)_3\overset{v}{N}\begin{matrix}\diagup CH_2.CO\\ \diagdown O\diagup\end{matrix} + H_2O.$$

Trimethyl Glycocoll.

Its hydrochloride is obtained directly by synthesis, when trimethylamine is heated with monochloracetic acid :—



$$(CH_3)_3N + CH_2Cl.CO.OH = (CH_3)_3\overset{v}{N}\begin{matrix}\diagup CH_2.CO.OH\\ \diagdown Cl\end{matrix},$$

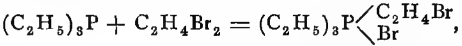
and on heating amidoacetic acid (glycocoll), $NH_2.CH_2.COOH$, with methyl iodide, caustic potash and wood spirit.

Betaïne occurs already formed in the sugar-beet (*Beta vulgaris*), hence, is present in the molasses from the beet. It crystallizes from alcohol with one molecule of water in shining crystals, which deliquesce in the air, has an alkaline reaction and a sweetish taste. At 100° it loses one molecule of water. When boiled with alkalies it decomposes, liberating trimethylamine.

PHOSPHORUS BASES.

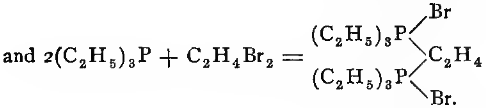
A number of diphosphines are derived from phosphine; they are perfectly analogous to the diamines (p. 157).

When triethylphosphine acts upon ethylene bromide we obtain :—



$$(C_2H_5)_3P + C_2H_4Br_2 = (C_2H_5)_3P \begin{matrix} \diagup C_2H_4Br \\ \diagdown Br \end{matrix},$$

Triethyl-bromethyl-phosphonium Bromide.



$$\text{and } 2(C_2H_5)_3P + C_2H_4Br_2 = \begin{matrix} & \diagup Br \\ (C_2H_5)_3P & \\ & \rangle C_2H_4 \\ (C_2H_5)_3P & \\ & \diagdown Br. \end{matrix}$$

Hexethyl-ethylene-diphosphonium Bromide.

The phosphonium bases are set free by the action of silver nitrate or oxide upon the preceding compounds.

Triethyl arsine, $As(C_2H_5)_3$, forms similar derivatives with ethylene bromide.

SULPHONIC ACIDS OF THE DIVALENT RADICALS (p. 152).

Methene Disulphonic Acid, $CH_2 \begin{matrix} \diagup SO_3H \\ \diagdown SO_3H \end{matrix}$, **Methionic Acid,** is obtained by acting on acetamide or methyl cyanide with fuming sulphuric acid. The acid forms long, deliquescent needles. The *barium salt*, $CH_2(SO_3)_2Ba + 2H_2O$, occurs in pearly leaflets, and is sparingly soluble in water. Barium chloride precipitates it from a solution of the acid. The free acid is very stable and not decomposed when boiled with HNO_3.

Hydroxymethene Sulphonic Acid, $CH_2 \begin{matrix} \diagup OH \\ \diagdown SO_3H \end{matrix}$, or oxy-methyl sulphonic acid, $CH_2(OH).SO_3H$, is formed when SO_3 acts upon methyl alcohol, and the product is boiled with water. Very likely a compound is first produced in this reaction which is analogous to ethionic acid (p. 319). It crystallizes with difficulty and is very stable. The *barium salt* crystallizes in small anhydrous plates.

In addition to the preceding acid we have oxymethene disulphonic acid, $CH(OH) \begin{matrix} \diagup SO_3H \\ \diagdown SO_3H \end{matrix}$, and methine trisulphonic acid, $CH(SO_3H)_3$.

Ethylene Disulphonic Acid, $C_2H_4 \begin{matrix} \diagup SO_3H \\ \diagdown SO_3H \end{matrix}$, is produced by oxidizing glycol mercaptan and ethylene sulphocyanate with concentrated nitric acid; by acting upon alcohol or ether with fuming sulphuric acid; and by boiling ethylene bromide with a concentrated solution of potassium sulphite:—

$$C_2H_4Br_2 + 2KSO_2.OK = C_2H_4\left\langle\begin{array}{l}SO_2.OK\\SO_2.OK\end{array}\right. + 2KBr.$$

The acid is a thick liquid, readily soluble in water, and crystallizes with difficulty. When it yields crystals these fuse at 94°. The *barium salt*, $C_2H_4(SO_3)_2Ba$, crystallizes from water in six-sided plates. **Ethylene Disulphinic Acid,** $C_2H_4(SO_2H)_2$, results from the reduction of ethylene disulphonic acid.

Hydroxyethylene Sulphonic Acid, $\begin{array}{l}CH_2.OH\\|\\CH_2.SO_3H\end{array}$, **Isethionic Acid,** oxyethysulphonic acid, $C_2H_4(OH).SO_3H$, is isomeric with ethyl sulphuric acid, $SO_4H(C_2H_5)$, and is produced by oxidizing monothioethylene glycol, $C_2H_4\left\langle\begin{array}{l}OH\\SH\end{array}\right.$, with HNO_3; by the action of nitrous acid upon taurine (below):—

$$C_2H_4\left\langle\begin{array}{l}NH_2\\SO_3H\end{array}\right. + NO_2H = C_2H_4\left\langle\begin{array}{l}OH\\SO_3H\end{array}\right. + N_2 + H_2O;$$

by heating ethylene chlorhydrin with potassium sulphite:—

$$C_2H_4\left\langle\begin{array}{l}OH\\Cl\end{array}\right. + KSO_3K = C_2H_4\left\langle\begin{array}{l}OK\\SO_3K\end{array}\right. + KCl;$$

and further by boiling ethionic acid (p. 319) with water.

Preparation.—Conduct the vapors of SO_3 into strongly cooled, anhydrous alcohol or ether, dilute with water and then boil for several hours. The fluid will contain isethionic, sulphuric, and some methionic acids. It is next saturated with barium carbonate, and the barium sulphate removed by filtration. When the solution is evaporated barium methionate crystallizes out first, and after further concentration barium isethionate (*Berichte*, 14, 64, and *Annalen*, 223, 198).

Isethionic acid is obtained as a thick liquid, which solidifies when allowed to stand over sulphuric acid. Being a sulphonic acid, it is not decomposed when boiled with water. Its salts are very stable and crystallize well.

The *barium salt* is anhydrous. The *ammonium salt* forms rhombic plates, which fuse at 135°, and at 210–220° it changes to di-isethionic acid (*Berichte*, 14, 65). *Ethyl isethionate*, $C_2H_4(OH).SO_3.C_2H_5$, boils at 120°, and is formed in the distillation of the diethyl sulphuric ester (p. 149; see *Berichte*, 15, 947). Chromic acid oxidizes the isethionic acid to sulpho-acetic acid.

PCl_5 converts the acid or its salts into the *chloride*, $C_2H_4\left\langle\begin{array}{l}Cl\\SO_2.Cl\end{array}\right.$, a liquid, boiling at 200°. When it is boiled with water it is converted into chlorethylsulphonic acid, $CH_2Cl.CH_2.SO_3H$ (*Annalen*, 223, 212).

Taurine, $C_2H_7NSO_3$, Amido-ethylsulphonic acid, $\begin{array}{l}CH_2.NH_2\\ |\\ CH_2.SO_3H\end{array}$, occurs as taurocholic acid, in combination with cholic acid, in the bile of oxen and many other animals, and also in the different animal secretions. It can be artificially prepared by heating chlorethylsulphonic acid, $CH_2Cl.CH_2.SO_3H$ (from isethionic acid with PCl_5), with aqueous ammonia and by the union of vinylamine (p. 163) with sulphurous acid, when they are evaporated together:—

$$C_2H_3NH_2 + SO_3H_2 = C_2H_4\Big\langle\begin{matrix}NH_2\\SO_3H\end{matrix} \quad (\textit{Berichte}, 21, 2667).$$

Taurine crystallizes in large, monoclinic prisms, insoluble in alcohol, but readily dissolved by hot water. It melts and decomposes about 240°.

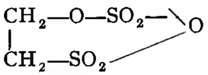
Taurine contains the groups NH_2 and SO_3H, and is, therefore, both a base and a sulphonic acid. But as the two groups neutralize each other the compound has a neutral reaction. It can, however, form salts with the alkalies. It separates unaltered from its solution in acids (see Glycocoll).

Nitrous acid converts it into isethionic acid (p. 318). Boiling alkalies and acids do not affect it, but when fused with caustic potash it breaks up according to the equation:—

$$C_2H_4\Big\langle\begin{matrix}NH_2\\SO_3K\end{matrix} + 2KOH = C_2H_3KO_2 + SO_3K_2 + NH_3 + H_2.$$

By introducing methyl into taurine we obtain tauro-betaïne, analogous to betaïne (p. 316): $(CH_3)_3.\overset{v}{N}\Big\langle\begin{matrix}C_2H_4\\O\end{matrix}\Big\rangle SO_2$.

Carbyl Sulphate, $C_2H_4S_2O_6$ (*Annalen,* 213, 210), is formed when the vapors of SO_3 are passed through anhydrous alcohol. It is the anhydride of ethionic acid:—



Carbyl Sulphate.

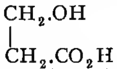
$$\begin{array}{l}CH_2—O—SO_2.OH\\ \cdot\\ CH_2—SO_2.OH.\end{array}$$

Ethionic Acid.

It is also produced in the direct union of ethylene with two molecules of SO_3. It is a deliquescent, crystalline mass, fusing at 80°. With water it yields **Ethionic Acid,** $C_2H_4\Big\langle\begin{matrix}O.SO_3H\\SO_3H\end{matrix}$. The constitution of the latter would indicate it to be both a sulphonic acid and primary sulphuric ester. It is therefore dibasic, and on boiling with water readily yields sulphuric and isethionic acids:—

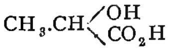
$$C_2H_4\Big\langle\begin{matrix}O.SO_3H\\SO_3H\end{matrix} + H_2O = C_2H_4\Big\langle\begin{matrix}OH\\SO_3H\end{matrix} + SO_4H_2.$$

Ethidene Sulphonic Acids. The following grouping is intended to express the relations of the sulphonic acids of this group with those of ethylene and the corresponding carboxylic acids:—



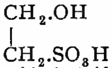
$$\begin{array}{l}CH_2.OH\\|\\CH_2.CO_2H\end{array}$$

Ethylene Lactic Acid.



$$CH_3.CH\left\langle\begin{matrix}OH\\CO_2H\end{matrix}\right.$$

Ethidene Lactic Acid.

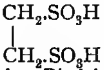


$$\begin{array}{l}CH_2.OH\\|\\CH_2.SO_3H\end{array}$$

Isethionic Acid.

$$CH_3.CH\left\langle\begin{matrix}OH\\SO_3H\end{matrix}\right.$$

Ethidene-hydroxy-sulphonic Acid.

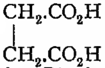


$$\begin{array}{l}CH_2.SO_3H\\|\\CH_2.SO_3H\end{array}$$

Ethylene Disulphonic Acid.

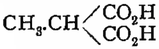
$$CH_3.CH\left\langle\begin{matrix}SO_3H\\SO_3H\end{matrix}\right.$$

Ethidene-disulphonic Acid.



$$\begin{array}{l}CH_2.CO_2H\\|\\CH_2.CO_2H\end{array}$$

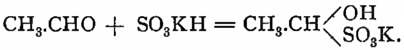
Ethylene Dicarboxylic Acid.
Succinic Acid.



$$CH_3.CH\left\langle\begin{matrix}CO_2H\\CO_2H\end{matrix}\right.$$

Ethidene Dicarboxylic Acid.
Isosuccinic Acid.

The compounds formed by the union of aldehydes with alkaline sulphites (p. 189), are viewed as salts of ethidene-hydroxy-sulphonic acid:—



$$CH_3.CHO + SO_3KH = CH_3.CH\left\langle\begin{matrix}OH\\SO_3K.\end{matrix}\right.$$

The *potassium salt* is anhydrous and forms needles; the *sodium salt*, $C_2H_4(OH).SO_3Na + H_2O$, consists of shining leaflets. When these are heated with water they decompose into aldehyde, water and sulphites.

Ethidene Chlorsulphonic Acid, $CH_3.CH\left\langle\begin{matrix}Cl\\SO_3H\end{matrix}\right.$, α-chlorethyl sulphonic acid, is obtained by heating ethidene chloride to 140° with aqueous neutral sodium sulphite. The acid is quite stable; its salts crystallize well. The sodium salt forms pearly leaflets.

Ethidene Disulphonic Acid, $CH_3.CH(SO_3H)_2$, results when thioaldehyde, or thialdine, is oxidized with MnO_4K. It forms very stable salts (*Berichte*, 12, 682). When ethyl iodide acts upon its silver salt the product is the *diethyl ester*, $CH_3.CH(SO_3.C_2H_5)_2$. This is an oil, insoluble in water and caustic soda. The hydrogen of its CH-group can be exchanged for sodium by the action of sodium alcoholate and then by alkyls. Herein it resembles sulpho-acetic ester and malonic ester, (p. 262) (*Berichte*, 21, 1551).

ALDEHYDE ALCOHOLS.

These contain both an alcoholic hydroxyl group and the aldehyde group CHO, hence their properties are both those of alcohols and aldehydes (p. 296). The addition of 2 H-atoms changes them to glycols, while by oxidation they yield the oxy-acids.

(1) *Glycolyl Aldehyde*, $CH_2(OH).CHO$, may be considered the first aldehyde of glycol, and glyoxal (p. 324) the second or dialdehyde.

(2) **Aldol**, $C_4H_8O_2 = CH_3.CH(OH).CH_2.CHO$, β-oxybutyraldehyde. This is obtained by letting dilute hydrochloric acid act upon crotonaldehyde (p. 199) and acetaldehyde:—

$$CH_3.CHO + CH_3.CHO = CH_3.CH(OH).CH_2.CHO.$$

A mixture of acetaldehyde and dilute hydrochloric acid, prepared in the cold, is permitted to stand 2–3 days, at a medium temperature, until it has acquired a yellow color. It is then neutralized with sodium carbonate, shaken with ether, the latter evaporated, and the residual aldol distilled in a vacuum (*Berichte*, 14, 2069).

Aldol is a colorless, odorless liquid, with a specific gravity of 1.120 at 0°, and is miscible with water. Upon standing it changes to a sticky mass, which cannot be poured. Aldol distils in a vacuum undecomposed at 100°; but under atmospheric pressure it loses water and becomes crotonaldehyde:—

$$CH_3.CH(OH).CH_2.CHO = CH_3.CH:CH.CHO + H_2O.$$

As an aldehyde it will reduce an ammoniacal silver nitrate solution. Heated with silver oxide and water it yields β-oxybutyric acid, $CH_3.CH(OH).CH_2.CO_2H$.

On standing it polymerizes into *paraldol*, $(C_4H_8O_2)_n$, which melts at 80–90°. Should the mixture of aldehyde and hydrochloric acid used for the preparation of aldol stand for some time, water separates, and we obtain the so-called *dialdan*, $C_8H_{14}O_3$. This melts at 139°, and reduces ammoniacal silver solutions.

Ammonia converts aldol in ethereal solution into aldol-ammonia, $C_4H_8O_2.NH_3$, a thick syrup, soluble in water. When heated with ammonia we get the bases, $C_8H_{15}NO_2$, $C_8H_{13}NO$ (oxytetraldin, p. 199) and $C_8H_{11}N$ (collidine). With aniline aldol forms methyl quinoline.

KETONE-ALCOHOLS.

These compounds contain both the ketone and alcohol groups. A simpler designation for them is *ketols*. They are distinguished, with reference to the relative position of the two groups, as α-, β-, γ-, or (1.2)-, (1.3)-, etc., ketols (compare diketones, p. 325) (*Berichte*, 22, 2114). Being ketones, the ketols unite with the primary alkaline sulphites, with phenylhydrazine, etc.

Acetyl Carbinol, Methyl Ketol, Acetol, $CH_3.CO.CH_2.OH$, is only known in aqueous solution. It is obtained from monobromacetone by the action of silver oxide or potassium carbonate, and by fusing cane and grape sugar with caustic alkali (*Berichte*, 16, 837). Acetol, its ethyl ether, and its esters may be formed from the corresponding propargylic compounds by hydration with $HgBr_2$ (p. 87):—

$$CH \vdots C.CH_2.OH + H_2O = CH_3.CO.CH_2.OH.$$

Its solution reduces alkaline copper solutions even in the cold. The *ethyl ether*, $C_3H_5O.O.C_2H_5$, boils at 128°. It is produced by the action of sodium upon chloracetic acid. Its phenylhydrazone yields an indol derivative when heated (*Berichte*, 21, 2649). The *acetyl ester*, $C_3H_5O.O.C_2H_3O$, is obtained from chloracetone, $CH_3.CO.CH_2Cl$, by heating the latter with potassium acetate and alcohol. It boils at 172°, and is readily soluble in water. The *benzoyl ester*, $C_3H_5O.O.C_7H_5O$, melts at 24°. The esters reduce warm alkaline copper solutions, forming α-lactic acid (*Berichte*, 13, 2344):—

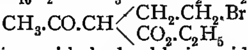
$$\underset{\text{Acetol.}}{CH_3.CO.CH_2.OH} + O = \underset{\alpha\text{-Lactic Acid.}}{CH_3.CH(OH).CO.OH.}$$

Acetol combines with 2 molecules of phenylhydrazine and forms the osazone, $CH_3.C(N_2H.C_6H_5).CH(N_2H.C_6H_5)$ (see the osazones, and *Berichte*, 21, Ref. 98). In this respect it resembles the glucoses.

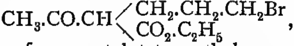
Homologous Acetols, $R.CO.CH_2.OH$, have been obtained as ethers from the halogen derivatives of alkylized acetoacetic esters (*Berichte*, 21, 2648).

Acetyl-methyl Carbinol, $C_4H_8O_2 = CH_3.CH(OH).CO.CH_3$, or **Dimethyl Ketol**, corresponds to benzoin of the aromatic series. It is prepared by reducing diacetyl (p. 326) with zinc and sulphuric acid. It is a liquid, boiling at 142°. It is miscible with water, and reduces Fehling's solution. It yields the osazone of diacetyl (*Berichte*, 22, 2214) when heated with phenylhydrazine.

The following is a γ-, or (1.3)-Ketol:—

Acetopropyl Alcohol, $C_5H_{10}O_2 = CH_3.CO.CH_2.CH_2.CH_2OH$, is obtained from bromethyl acetoacetic ester,  $CH_3.CO.CH\left\langle\begin{matrix}CH_2.CH_2.Br\\ CO_2.C_2H_5\end{matrix}\right.$ (from acetyl trimethylene carboxylic ester), upon boiling with hydrochloric acid. It is a mobile liquid, of peculiar odor, and boils at 208°. It does not reduce either an ammoniacal silver solution or Fehling's solution. When slowly distilled it separates into water and an *anhydride* (a pleasant-smelling liquid, boiling about 75°). The latter can be considered a methyl-dihydrofurfurane, $C_4H_5(CH_3)O$. Acetopropyl alcohol yields a hydrazone anhydride with phenylhydrazine. Chromic acid oxidizes it to lævulinic acid (*Berichte*, 21, 1196; 22, Ref. 572).

Hydrobromic acid converts the alcohol into *brom-propyl-methyl ketone*, $CH_3.CO.CH_2.CH_2CH_2Br$. This, like the γ-diketones (p. 328), yields a pyrrol derivative when heated with ammonia (*Berichte*, 19, 2844).

Acetobutyl Alcohol, $C_6H_{12}O_2 = CH_3.CO.C_3H_6.CH_2.OH$, is obtained by boiling brom-propyl acetoacetic ester,  $CH_3.CO.CH\left\langle\begin{matrix}CH_2.CH_2.CH_2Br\\ CO_2.C_2H_5\end{matrix}\right.$, with hydrochloric acid (*Berichte*, 18, 3277); also from acetyl tetramethylene carboxylic ester (*Berichte*, 19, 2558). It is a liquid, very soluble in water, alcohol and ether, and has an odor resembling that of camphor. It boils about 155°. It does not reduce either an ammoniacal silver solution, or Fehling's solution. Sodium amalgam converts it into δ-hexylene glycol (p. 310); while chromic acid oxidizes it to γ-acetobutyric acid. Boiling HBr-acid converts it into *brom-butylmethyl ketone*, $CH_3.CO.C_3H_6.CH_2Br$. This is a liquid, boiling at 216°. It forms a pyridine derivative (tetrahydropicoline) (*Berichte*, 19, 2844), when heated with ammonia. In this respect it is like the δ-diketones.

Diacetone Alcohol, $C_6H_{12}O_2 = CH_3.CO.CH_2.C(CH_3)_2OH$, is obtained from diacetonamine (p. 208) by the action of nitrous acid. A liquid, miscible with water, alcohol and ether. Specific gravity = 0.930 at 25°. It boils at 164°. Mixed with sulphuric acid it parts with water and becomes mesityl oxide (p. 208).

KETON-ALDEHYDES.

Pyroracemic Aldehyde, $CH_3.CO.CHO$, **Acetyl-formyl** or **Methyl Glyoxal**, is obtained by boiling isonitroso-acetone (p. 206) with dilute sulphuric acid (this is analogous to the formation of the α-diketones, p. 325). Hydroxylamine is split off in this reaction (see the oximes, p. 202):—

$$CH_3.CO.CH{:}N.OH + H_2O = CH_3.CO.CHO + NH_2.OH;$$

a volatile yellow oil. It reduces an ammoniacal silver solution. It forms a hydrazone very readily (*Berichte*, 20, 3218). It yields an osazone, $C_{15}H_{18}N_4$, with 2 molecules of phenylhydrazine; the same compound is obtained from acetol (p. 321). (*Berichte*, 21, Ref. 98).

β-**Keton-aldehydes**, general formula $R.CO.CH_2.COH$, are synthetically prepared by the interaction of ketones, $R.CO.CH_3$, and formic acid esters, in the presence of sodium alcoholate. The sodium compounds first result (Claisen, *Berichte*, 20, 2191; 21, Ref. 915; 22, 3273):—

$$R.CO.CH_3 + \underset{\text{Formic Ester.}}{CHO.O.C_2H_5} + NaO.C_2H_5 = R.CO.CHNa.CHO + 2C_2H_5OH.$$

The ketones $R.CO.CH_2R$ react similarly with these esters, but not those of the type $R.CO.CHR_2$. This is explained by assuming that an earlier union occurs between the acid ester and sodium ethylate (*Berichte*, 22, 533).

The keton-aldehydes, $R.CO.CH_2.CHO$, and $R.CO.CHR.CHO$, like the β-diketones, $R.CO.CH_2.CO.R$, are acid in their nature. The hydrogen of the groups CH_2 and CHR is readily replaced by metals. They dissolve in alkaline carbonates to form salts, *e. g.*, $R.CO.CHNa.CHO$. They produce green-colored precipitates with copper acetate (*Berichte*, 22, 1018). Ferric chloride imparts a deep violet or red color to their alcoholic solutions (*Berichte*, 22, 3277). They readily yield oximes, anilides, benzene azo-derivatives (*Berichte*, 21, 1699), hydrazones, pyrrazoles, isoxazoles, etc.

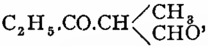
The keton-aldehydes, $R.CO.CH_2.CHO$, are very unstable when free. They condense readily. Their sodium and other salts are, however, very stable. The monoalkylic keton-aldehydes, $R.CO.CHR.CHO$, are so constituted that they cannot sustain analogous condensation, hence they are stable when in a free condition, and can generally be distilled (*Berichte*, 22, 3274).

Acetyl aldehyde, $CH_3.CO.CH_2.CHO$, *Formyl acetone*, from acetone and formic ester, is a liquid, boiling near 100°. Its odor resembles that of acetoacetic ester and of acetone. Ferric chloride colors it a deep red. It readily condenses, even in solution, to triacetyl benzene:—

$$3CH_3.CO.CH_2.CHO = C_6H_3(CO.CH_3)_3 + 3H_2O.$$

It forms methyl-phenyl-pyrrazole with phenylhydrazine (*Berichte*, 21, 1144).

Propionyl Aldehyde, $C_2H_5.CO.CH_2.CHO = C_5H_8O_2$, *formyl methyl-ethyl ketone*, results from methyl-ethyl ketone and formic ester. It yields ethyl-phenyl pyrrol with phenylhydrazine.

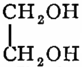


Propionyl-propionic Aldehyde, $C_6H_{10}O_2 = C_2H_5.CO.CH\left\langle\begin{matrix}CH_3\\CHO\end{matrix}\right.$, *formyl diethyl ketone*, from diethylketone, is stable when free (see above). It consists of crystals having a peculiar odor. They melt at 40°. For additional keton-aldehydes consult *Berichte* 22, 3277.

DIALDEHYDES.

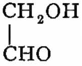
The only known dialdehyde of the fat series is glyoxal.

Glyoxal, $C_2H_2O_2 = CHO.CHO$, Diformyl, is the dialdehyde of ethylene glycol, while glycolyl aldehyde (p. 321) represents the first or half aldehyde:—



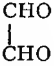
$$\begin{array}{l} CH_2OH \\ | \\ CH_2OH \end{array}$$

Glycol.



$$\begin{array}{l} CH_2OH \\ | \\ CHO \end{array}$$

Glycolyl Aldehyde.



$$\begin{array}{l} CHO \\ | \\ CHO \end{array}$$

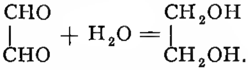
Glyoxal.

Glyoxal, glycollic acid and glyoxylic acid are formed in the careful oxidation of ethylene glycol, ethyl alcohol, or acetaldehyde with nitric acid.

In preparing glyoxal, alcohol, or better, aldehyde and fuming nitric acid are placed, layer after layer, in narrow glass cylinders, using a funnel tube for the introduction of the acid. Let the whole stand for 5–6 days (*Berichte*, 14, 2685). The residue obtained by evaporation of the mixture to syrup consistence contains chiefly glyoxal, with a little glycollic acid and glyoxylic acid. These can be removed in the form of calcium salts. To obtain the glyoxal, the residue is directly treated with a concentrated solution of primary sodium sulphite, when the double salt with glyoxal (see below) will crystallize out (*Berichte*, 17, 169).

On evaporating the solutions the glyoxal is obtained as an amorphous, non-volatile mass. It deliquesces in the air. It is very soluble in both alcohol and ether. In this condition it is probably a polymeric modification $(C_2H_2O_2)_2$, because methylglyoxal (p. 323) and dimethyl glyoxal (p. 326) are very volatile (*Berichte*, 21, 809). The alkalies convert it, even in the cold, into glycollic acid.

In this change the one CHO group is reduced, while the other is oxidized (compare benzil and benzilic acid):—



$$\begin{array}{l} CHO \\ | \\ CHO \end{array} + H_2O = \begin{array}{l} CH_2OH \\ | \\ CH_2OH. \end{array}$$

As a dialdehyde it unites directly with 2 molecules of primary sodium sulphite, forming the crystalline compound, $C_2H_2O_2(SO_8HNa)_2 + H_2O$. It also reduces ammoniacal silver solutions.

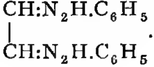
With ammonium cyanide and hydrochloric acid, glyoxal forms diamido-succinic acid (p. 190). It also yields a dioxime with two molecules of hydroxylamine; this is the so-called **Glyoxime**, CH(N.OH).CH(N.OH) (p. 207). This is also produced when hydroxylamine acts upon trichlorlactic acid (*Berichte*, 17, 2001). It is soluble in water, alcohol and ether. It crystallizes in rhombic plates, melts at 178°, and sublimes without difficulty. It has a faintly acid reaction and forms salts with the bases.

As to the deportment of other dialdehydes towards hydroxylamine see *Berichte*, 20, 507.

See *Berichte*, 21, Ref. 636, for the compounds of glyoxal with malonic and acetoacetic esters.

Glyoxal combines with 2 molecules of phenylhydrazine and yields—

Glyoxal Diphenyl Hydrazine,



$$\begin{array}{l} CH{:}N_2H.C_6H_5 \\ | \\ CH{:}N_2H.C_6H_5 \end{array}.$$

This derivative can also

be prepared from trichlorlactic acid (*Berichte*, 17, 2001). It crystallizes in needles or leaflets, melting at 170°. Its HCl-salt is a yellow-colored compound (*Berichte*, 19, Ref. 303).

Glyoxal and orthophenylene diamines unite and form quinoxaline derivatives (see these).

Concentrated ammonia yields two bases with glyoxal: **Glycosin**, $C_6H_6N_4$, of unknown constitution, and in larger quantity, **Glyoxaline**, $C_3H_4N_2$, the parent substance of the glyoxalines (oxalines), or amidazoles (β-diazoles) (see these).

Malonyl Aldehyde, $CH_2\left\langle\begin{array}{l}CHO\\CHO\end{array}\right.$, and **Succinyl Aldehyde**, $\begin{array}{l}CH_2.CHO\\|\\CH_2.CHO\end{array}$, have not been obtained. They are the aldehydes of tri- and tetramethylene glycols.

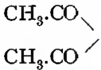
Succinyl Aldoxime, $\begin{array}{l}CH_2.CH(N.OH)\\|\\CH_2.CH(N.OH)\end{array}$, results from the action of hydroxylamine upon pyrrol. It yields tetramethylene diamine when reduced with metallic sodium (p. 313) (*Berichte*, 22, 1968).

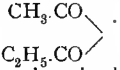
DIKETONES.

The diketones contain two ketone groups, — CO. The relative position of these groups determines them to be either α-, β-, or γ-diketones, etc. Peculiar characteristics distinguish these classes.

(1) α-**Diketones**, $R.CO.CO.CH_3$.

The α-, (or 1.2)-diketones have their two CO-groups united directly to each other. In the aromatic series they are called orthodiketones (see these). They may be regarded as diketo-substituted ethanes. Hence, the name αβ-diketo-butane for the compound, $CH_3.CO.CO.CH_3$ (see p. 201); or they can be viewed as compounds of two acid radicals (that cannot exist uncombined) (p. 246):—


Diacetyl.


Acetyl-propionyl.

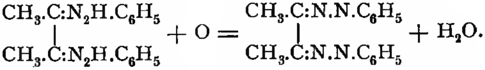
The α-diketones are prepared by boiling the isonitrosoketones (same as acetyl formyl from isonitrosoacetone, p. 323) with dilute sulphuric acid (p. 206) (v. Pechmann, *Berichte*, 20, 3213):—

$$CH_3.CO.C(N.OH).CH_3 + H_2O = CH_3.CO.CO.CH_3 + NH_2.OH.$$

The solutions obtained by the action of nitrous acid upon mono-alkyl-acetoacetic esters may be used for this purpose, instead of the prepared nitrosoketones (*Berichte*, 21, 1411). At times nitrous acid effects the decomposition more rapidly than sulphuric acid (*Berichte*, 22, 532, 527).

The α-diketones are yellow-colored, volatile liquids. They possess a penetrating odor. They yield *monoximes* with one molecule of hydroxylamine. These compounds are also called *ketoximes* (*Berichte*, 21, 2994). With 2 molecules of hydroxylamine they form the *dioximes* (glyoximes or acetoximic acids, p. 203). These can form anhydrides (see benzildioxime or diphenylglyoxime). The α-diketones with 1 molecule of phenylhydrazine yield *monohydrazones* (or ketohydrazones), and with 2 molecules of phenylhydrazine the *dihydrazones*, called also *osazones*.*

The osazones are bright red, crystalline compounds. When digested with alcohol and ferric chloride they produce reddish-brown colorations, soluble in ether (reaction of Pechmann). Oxidation takes place and the *osotetrazones* result:—

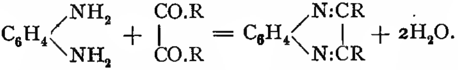


$$\begin{array}{l}CH_3.C{:}N_2H.C_6H_5\\ \quad |\\ CH_3.C{:}N_2H.C_6H_5\end{array} + O = \begin{array}{l}CH_3.C{:}N.N.C_6H_5\\ \quad |\\ CH_3.C{:}N.N.C_6H_5\end{array} + H_2O.$$

These split off one phenyl group and pass into the *osotriazones* (*Berichte*, 21, 2751).

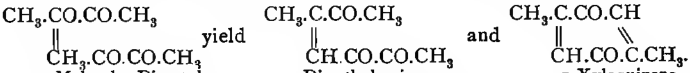
The *hydrazoximes*, *e. g.*, $CH_3.C(N.OH).C(N_2H.C_6H_5).CH_3$, diacetyl hydrazoxime, are compounds of the diketones with 1 molecule of hydroxylamine and 1 molecule of phenylhydrazine. They form when phenylhydrazine acts upon the mon-oximes, or hydroxylamine upon the mono-hydrazones (or ketohydrazones) (*Berichte*, 21, 2994).

The α-diketones are characterized and distinguished from the β-, and γ-ketones by their ability to unite with the orthophenylene diamines (similar to glyoxal). In this way they are condensed to the *quinoxalines* (see these):—



$$C_6H_4\begin{array}{l}\diagup NH_2\\ \diagdown NH_2\end{array} + \begin{array}{l}CO.R\\ |\\ CO.R\end{array} = C_6H_4\begin{array}{l}\diagup N{:}CR\\ \qquad |\\ \diagdown N{:}CR\end{array} + 2H_2O.$$

All compounds containing the group —CO.CO—, *e. g.*, glyoxal, pyroracemic acid, glyoxylic acid, alloxan, dioxytartaric acid, etc., react similarly with the *o*-phenylene diamines. The *glyoxalines* are the products of the union of the α-diketones with ammonia and the aldehydes. α-Diketones, containing a CH_2-group, together with the CO-group, sustain a rather remarkable condensation when acted upon by the alkalies. *Quinogens* are first produced, and later the *quinones* (*Berichte*, 21, 1418; 22, 2215):—



$$\begin{array}{l}CH_3.CO.CO.CH_3\\ \|\\ CH_3.CO.CO.CH_3\end{array} \text{ yield } \begin{array}{l}CH_3.C.CO.CH_3\\ \|\\ CH.CO.CO.CH_3\end{array} \text{ and } \begin{array}{l}CH_3.C.CO.CH\\ \| \qquad \diagdown\diagdown\\ CH.CO.C.CH_3.\end{array}$$

2 Molecules Diacetyl. Dimethyl-quinogen. p-Xyloquinone.

(1) **Diacetyl, $CH_3.CO.CO.CH_3$, Diketobutane, Dimethyl diketone,** from isonitrosomethylacetone or methyl acetoacetic ester (p. 209) (*Berichte*, 21, 1411), has also been obtained from oxalyldiacetic acid (ketipic acid) by the splitting-off of the carboxyls upon the application of heat (*Berichte*, 20, 3183). It is a yellow liquid, with an odor like that of quinone. It boils at 87–89°. It dissolves rather readily in water, and is miscible with both alcohol and ether. Sulphurous acid decolorizes the yellow solution. HCl-hydroxylamine precipitates the *dioxime*, $C_4H_6(N.OH)_2$; this melts at 234°. The *monophenylhydrazone*, $C_4H_6O(N_2H.C_6H_5)$, is also formed from methyl acetoacetic acid and benzene diazochloride. It melts at 133°. The *dihydrazone*, $C_4H_6(N_2H.C_6H_5)_2$ (see above), melts at 242°. It has been obtained from the hydrazone of pyroracemic acid (*Berichte*, 21, 549).

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* The α-aldehyde alcohols and α-keton alcohols (p. 321) yield similar osazones with 2 molecules of phenylhydrazine. An atom of oxygen from the air acts at the same time (just as with the osazones of the glucoses).

Two molecules of CNH convert diacetyl into *dicyanhydrin*, $C_4H_6(OH)_2(CN)_2$ (see p. 202). The latter yields dimethyl racemic acid (*Berichte*, 22, Ref. 137).

Tetrachlor-diacetyl, $CHCl_2.CO.CO.CHCl_2$, results in the action of potassium chlorate upon chloranilic acid (together with tetrachloracetone, p. 205). It crystallizes in yellow plates, melting at 84°. It yields a quinoxaline derivative with o-phenylenediamine, and a dihydrazone with phenylhydrazine (*Berichte*, 22, Ref. 809; 23, Ref. 20).

Tetrabrom-diacetyl, $C_4H_2Br_4O_2$ (*Berichte*, 23, 35) and **Dibrom-diacetyl**, $(CH_2Br.CO)_2$, are produced by the action of bromine upon diacetyl.

(2) **Acetyl-propionyl**, $C_2H_5.CO.CO.CH_3$, **Methyl-ethyl-diketone**, from isonitroso-ethylacetone, or ethyl acetoacetic ester, is very similar to diacetyl. It boils at 108° (*Berichte*, 22, 2117).

Acetyl-butyryl or **Methyl-propyldiketone**, $C_3H_7.CO.CO.CH_3$, **Acetyl-isobutyryl**, etc., as well as the *mixed* α-diketones of the paraffin and aromatic series, are analogous compounds (*Berichte*, 22, 2127).

(2) β- (or 1.3)-Diketones, R.CO.CH₂.CO.R.

In these compounds the two carbonyls are separated by an intervening C-atom. They are frequently formed by the breaking down of acidyl-acetoacetic esters (see benzoyl acetone). The usual course is analogous to the reaction by which the keton-aldehydes (p. 323) are produced. It consists in the interaction of acetic esters and ketones in the presence of sodium ethylate, or better, metallic sodium (Claisen, *Berichte*, 22, 1009; 23, Ref. 40):—

$$CH_3.CO.CH_3 + \underset{\text{Ethyl Acetate.}}{C_2H_5.O.CO.CH_3} = \underset{\text{Acetyl Acetone.}}{CH_3.CO.CH_2.CO.CH_3} + C_2H_5.OH.$$

The β-diketones, like the β-ketonaldehydes (p. 323) have an acid character. An H-atom of the CH_2-group can be replaced by metals (this is similar to the β-ketonic esters). They are, therefore, soluble in caustic alkalies, forming alkali salts, and with copper acetate they generally yield precipitates of copper salts (*Berichte*, 22, 1017). Ferric chloride imparts an intense red color to their alcoholic solution. They combine with 1 molecule of hydroxylamine with the separation of two molecules of water. The products are the remarkable *oxime-anhydrides*. These belong to the so-called *oxyazoles* (see these, and *Berichte*, 21, 2178).

With phenylhydrazine the β-diketones (and all other compounds containing the groups —CO.CH₂.CO—) yield *pyrrazole* compounds (see these). Methylphenylhydrazine, however, converts them into hydrazones (*Berichte*, 22, Ref. 671).

Acetyl-acetone, $C_5H_8O_2 = CH_3.CO.CH_2.CO.CH_3$, **Diacetylmethane**, $(CH_3.CO)_2CH_2$, was first prepared by digesting acetyl chloride with $AlCl_3$ (*Berichte*, 22, 1009). It is most easily obtained by the action of metallic sodium upon acetone and acetic ester (*Berichte*, 23, Ref. 40). It is a colorless liquid, boiling at 137°, and very readily soluble in ether. It dissolves in the caustic alkalies, and splits up into acetone and acetic acid. Its copper salt, $(C_5H_7O_2)_2Cu$ (see above), is precipitated as a blue-colored, crystalline precipitate. Phenylhydrazine converts it into dimethylphenyl pyrrazole, and with diazobenzene-chloride yields an azo-derivative (*Berichte*, 21, 1699).

Acetyl-methyl-ethyl Ketone, $CH_3.CO.CH_2.CO.C_2H_5 = C_8H_{10}O_2$, acetyl-propionyl methane, from methylethyl ketone and acetic ester, boils at 158°. Its sp. gr. is 0.9538.

Acetyl-methylpropyl Ketone, $C_7H_{12}O_2 = CH_3.CO.CH_2.CO.C_3H_7$, acetyl-butyryl methane, boils at 161° (*Berichte*, 22, 1015).

Diacetylacetone, $CO\langle\begin{smallmatrix}CH_2.CO.CH_3\\CH_2.CO.CH_3\end{smallmatrix}$, is a β triketone. It apparently is formed from dimethylpyrone (*Berichte*, 22, 1570).

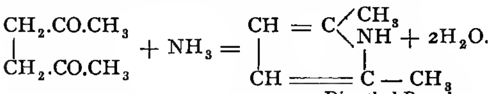
Oxalyldiacetone, $\begin{matrix}CO.CH_2.CO.CH_3\\|\\CO.CH_2.CO.CH_3\end{matrix}$, is an αβ-tetraketone. It is produced when sodium ethylate acts upon oxalic ester and acetone. It melts at 121° and dissolves easily in alcohol and ether. Ferric chloride colors it a brownish red (*Berichte*, 21, 1141).

3. γ-Diketones, $R.CO.CH_2.CH_2.CO.R$.

These correspond to the paraquinones of the aromatic series (see these). They are not capable of forming salts, hence are not soluble in the alkalies. They form mono- and di-oximes with hydroxylamine, and mono- and di-hydrazones with phenylhydrazine; these are colorless. The readiness with which the γ-diketones form pyrrol, furfurane, and thiophene derivatives is characteristic of them.

Acetonyl Acetone, $C_6H_{10}O_2 = CH_3.CO.CH_2.CH_2.CO.CH_3$, diacetylethane, is obtained from pyrotritartaric acid, $C_7H_8O_3$ (see this), and from acetonyl acetoacetic ester (p. 336), upon heating to 160° with water (*Berichte*, 18, 58), and from isopyrotritartaric acid, and diacetylsuccinic ester, when they are allowed to stand in contact with sodium hydroxide (*Berichte*, 22, 2100). A liquid with an agreeable odor. It is miscible with water, alcohol and ether. It boils at 188° C.

It unites to a *dioxime* with 2 molecules of hydroxylamine. This new derivative crystallizes in shining leaflets, melting at 136°. It is also produced by the action of hydroxylamine upon (1.4)-dimethylpyrrol (*Berichte*, 22, 3177). With 2 molecules of phenylhydrazine it yields a di-hydrazone, melting at 120°. Monophenylhydrazone, by the loss of 2 molecules of water, passes into a pyrrol derivative (*Berichte*, 22, 170). Dimethyl pyrrol is produced on heating acetonyl acetone with alcoholic ammonia (Paal, *Berichte*, 18, 58, 367):—



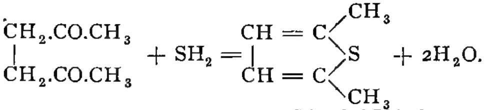
$$\begin{matrix}CH_2.CO.CH_3\\|\\CH_2.CO.CH_3\end{matrix} + NH_3 = \begin{matrix}CH = C\langle\begin{smallmatrix}CH_3\\NH\end{smallmatrix}\\|\qquad\quad|\\CH = C - CH_3\end{matrix} + 2H_2O.$$

Dimethyl Pyrrol.

All compounds containing two CO-groups in the (1.4) position react similarly with ammonia and amines. Such are diaceto-succinic ester and lævulinic ester. All the pyrrol derivatives formed as above, when boiled with dilute mineral acids, have the power of coloring a pine chip an intense red. This reaction is, therefore, a means of recognizing all (1.4)-diketone compounds (*Berichte*, 19, 46).

These derivatives react similarly with amidophenols and amido-acids (*Berichte*, 19, 558).

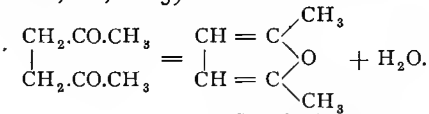
When heated with phosphorus sulphide acetonyl acetone yields dimethyl thiophene (Paal, *Berichte*, **18**, 2251):—



Dimethyl Thiophene.

All the γ-diketones or (1.4)-dicarboxyl compounds, *e. g.*, the γ-ketonic acids (p. 343), yield the corresponding thiophene derivatives upon like treatment (*Berichte*, **19**, 551).

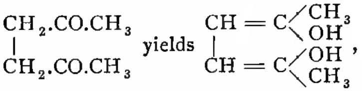
The direct removal of one molecule of water from acetonyl acetone (by distillation with zinc chloride or P_2O_5) affords dimethyl furfurane (*Berichte*, **20**, 1085):—



Dimethyl Furfurane.

Other γ-diketone compounds react in a similar manner (Knorr, *Berichte*, **17**, 2756).

In all these conversions of acetonyl acetone into pyrrol, thiophene, and furfurane derivatives it may be assumed that it first passes from the diketone form into the isomeric or tautomeric form of the unsaturated dihydroxyl (p. 54):—



and from this, by replacing the 2OH groups with S, O, or NH, the corresponding furfurane, thiophene and pyrrol compounds are produced (*Berichte*, **19**, 551).

(1.5) or δ-Diketones.

Derivatives of this class are produced when benzaldehyde acts upon esters of diazoacetic acid (*Berichte*, **18**, 2372) and upon acetoacetic ester (*Berichte*, **18**, 2583). They do not yield pyridine derivatives with ammonia.

ALDEHYDE ACIDS.

These are the compounds containing both the CHO and the CO_2H groups. Their properties are both those of the aldehyde and the acid. The only member of this class in the fat series is *Glyoxylic Acid.*

Glyoxylic Acid, $C_2H_2O_3 = \begin{array}{l}CHO\\ |\\ CO_2H\end{array}$ or $C_2H_4O_4 = \begin{array}{l}CH(OH)_2\\ |\\ CO.OH\end{array}$, *glyoxalic acid.* The aldehydes frequently yield hydrates by combining with one molecule of water; these derivatives are regarded as dihydroxyl compounds (see chloral hydrate, p. 196). Glyoxylic acid exhibits similar behavior. The free crystalline acid has the formula, $C_2H_2O_3.H_2O = C_2H_4O_4$; all its salts are obtained from it. Hence, we must consider it a dihydroxyl compound, which may be designated a dioxy-acetic acid. By withdrawal of water, the aldehyde group is produced, and the acid conducts itself as a true aldehyde acid.

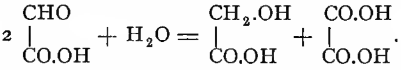
Glyoxylic acid is obtained by oxidizing glycol, alcohol and aldehyde (p. 324). It is most readily prepared by heating dichlor- and dibrom-acetic acid to 120° with water:—

$$CHCl_2.CO_2H + 2H_2O = CH(OH)_2.CO_2H + 2HCl.$$

It is a thick liquid, readily soluble in water, and crystallizes in rhombic prisms by long standing over sulphuric acid. The crystals have the formula, $C_2H_4O_4$. It distils undecomposed with steam.

As a monobasic acid it forms salts with one equivalent of acid. When dried at 100°, the salts have the formula, $C_2H_3MeO_4$. The ammonium salt alone has the formula, $C_2H(NH_4)O_3$. The calcium salt, $(C_2H_3O_4)_2Ca$, crystallizes with one and two molecules of water (*Berichte*, 14, 585), and is sparingly soluble in water (in 140 parts at 18°). Lime water precipitates an insoluble basic salt from its solution. The silver salt, $C_2H_3AgO_4$, is a white, crystalline precipitate.

Again, glyoxylic acid manifests all the properties of an aldehyde. It reduces ammoniacal silver solutions with formation of a mirror, and combines with primary alkali sulphites. When oxidized (silver oxide), it yields oxalic acid; by reduction (zinc and water) it forms glycollic acid: $CHO.CO_2H + H_2 = CH_2(OH.)CO_2H$. On boiling the acid or its salts with lime water, or alkalies, glycollic and oxalic acids are produced (*Berichte*, 13, 1392):—



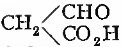
$$2\begin{array}{l}CHO\\ |\\ CO.OH\end{array} + H_2O = \begin{array}{l}CH_2.OH\\ |\\ CO.OH\end{array} + \begin{array}{l}CO.OH\\ |\\ CO.OH\end{array}.$$

This is analogous to the transposition of aldehydes to alcohol and acid (p. 189). When hydrocyanic and hydrochloric acids act upon glycollic acid, a like transposition ensues.

Phenylhydrazine unites with glyoxylic acid to phenyl-hydrazine-glyoxylic acid, $CH(N_2H.C_6H_5).CO_2H$ (*Berichte*, 17, 577).

Homologous β-aldehydic acids (their esters) are produced (analogous to the β-ketonic esters, p. 338) by the action of sodium, or sodium ethylate, upon a mixture of formic ester and acetic ester (or other esters) (Piutti, *Berichte*, 20, 537; W. Wislicenus, *Berichte*, 20, 2930):—

$$\underset{\text{Formic Ester.}}{CHO.O.C_2H_5} + \underset{\text{Acetic Ester.}}{CH_3.CO_2.C_2H_5} = \underset{\text{Formyl Acetic Ester.}}{CHO.CH_2.CO_2.C_2H_5} + C_2H_5.OH.$$

Formyl Acetic Acid,  $CH_2\begin{smallmatrix}\diagup CHO\\ \diagdown CO_2H\end{smallmatrix}$, may be called the half aldehyde of malonic acid, $CH_2(COOH)_2$. Its ethyl ester, from acetic and formic esters, is very unstable. It condenses immediately (analogous to the condensation of acetyl aldehyde to triacetyl benzene (p. 323) to the ester of trimesinic acid :—

$$3CHO.CH_2.CO_2.C_2H_5 = C_6H_3(CO_2.C_2H_5)_3 + 3H_2O$$

(*Berichte*, 21, 1146).

KETONIC ACIDS.

These contain both the groups CO and CO_2H; they, therefore, show acid and ketone characters with all the specific properties peculiar to these. In conformity with the manner of designating the mono- and di-substituted fatty acids (pp. 223 and 224), we distinguish the groups α-, β- and γ- of the ketonic acids. These differ from each other by various peculiarities:—

$R.CO.CO_2H$	$R.CO.CH_2.CO_2H$	$R.CO.CH_2.CH_2.CO_2H$.
α-Ketonic Acids.	β-Ketonic Acids.	γ-Ketonic Acids.

The α- and γ-acids are quite stable, even in a free condition. This is only the case with the β-acids when in the form of esters. If they are set free from these they readily decompose (p. 323).

The names of the ketonic acids are usually derived from the fatty acids, inasmuch as the acid radicals are introduced into these (p. 213); *e. g.*,—

$CH_3.CO.CO_2H$	$CH_3.CO.CH_2.CO_2H$, etc.
Acetyl-formic Acid.	Acetyl-acetic Acid.

According to a more recent suggestion of A. Baeyer, these acids should be viewed as *keto*-substitution products of the fatty acids, being formed by the substitution of oxygen for 2H in the CH_2-group (*Berichte*, 18, 160); hence the names:—

$CH_3.CO.CO_2H$	$CH_3.CO.CH_2.CO_2H$, etc.
α-Ketopropionic Acid.	β-Ketobutyric Acid.

In accord with their ketonic nature, they unite with alkaline sulphites to form crystalline compounds, from which alkalies or acids again set them free (*Berichte*, 17, Ref. 568). They form oximes or isonitroso fatty acids (p. 214) with hydroxylamine, and with phenyl-hydrazine phenyl-hydrazo-fatty acids. Nascent hydrogen converts all the ketonic acids into the corresponding divalent oxy-acids. In this change the ketonic group becomes a secondary alcohol group:—

$$CH_3.CO.CO_2H + H_2 = \underset{\text{α-Lactic Acid.}}{CH_3.CH(OH).CO_2H}.$$

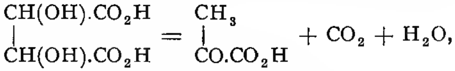
1. *a-Ketonic Acids*—$R.CO.CO_2H$.

In this class the ketone group CO is in direct union with the acid-forming carboxyl group, CO_2H. We can view them as compounds of acid radicals with carboxyl, or as derivatives of formic acid, HCO.OH, in which the hydrogen linked to carbon is replaced by an acid radical—hence the designation *acetyl carboxylic acid* or *acetyl formic acid* for the acid, $CH_3.CO.CO_2H$. The first name indicates, too, the general synthetic method of formation of these acids from the cyanides of acid radicals (p. 247), which, by the action of concentrated hydrochloric acid, are changed to the corresponding ketonic acids:—

$$\underset{\text{Acetyl Cyanide.}}{CH_3.CO.CN} + 2H_2O + HCl = \underset{\text{Acetyl Carboxylic Acid.}}{CH_3.CO.CO_2H} + NH_4Cl.$$

(1) **Pyroracemic Acid, α-Ketopropionic Acid** (acetyl carboxylic acid), $C_3H_4O_3 = CH_3.CO.CO_2H$, was first obtained in the distillation of racemic acid, tartaric acid and glyceric acid. It is synthetically prepared from α-dichlorpropionic acid, $CH_3.CCl_2.CO_2H$ (p. 225), when heated with water and silver oxide, and from acetyl cyanide by the action of hydrochloric acid (see above). Further, by the action of concentrated hydrochloric acid upon acetyl cyanide. Its formation in the oxidation of ordinary lactic acid with potassium permanganate, and by the decomposition of oxalacetic ester, is rather remarkable.

For its preparation heat tartaric acid in an iron pan until it chars and swells up. After cooling, the mass is broken into pieces, placed in a retort and distilled over a free flame (*Annalen*, 172, 142). A large yield (about 60 per cent.) is reached by distilling tartaric acid with potassium bisulphate (*Berichte*, 14, 321). The formation of pyroracemic acid from tartaric acid (racemic acid and glyceric acid):—



$$\begin{matrix}CH(OH).CO_2H\\ |\\ CH(OH).CO_2H\end{matrix} = \begin{matrix}CH_3\\ |\\ CO.CO_2H\end{matrix} + CO_2 + H_2O,$$

is quite similar to the transpositions cited on page 134.

Pyroracemic acid is a liquid, soluble in alcohol, water and ether, and has an odor quite similar to that of acetic acid. It boils at 165–170°, decomposing partially into CO_2 and pyrotartaric acid ($2C_3H_4O_3 = C_5H_8O_4 + CO_2$). This change is more readily effected if the acid be heated to 100° with hydrochloric acid.

The acid reduces ammoniacal silver solutions with the production of a silver mirror, the decomposition products being CO_2 and acetic acid. When heated with dilute sulphuric acid to 150° it splits up into CO_2 and aldehyde, $CH_3.COH$. This ready separation of aldehyde accounts for the ease with which pyroracemic acid enters into various condensations, *e.g.*, the formation of crotonic acid by the action of acetic anhydride (p. 238), and the condensations with dimethyl aniline and phenols (*Berichte*, 18, 987, and 19, 1089).

Pyruvic acid is monobasic. Its salts crystallize with difficulty. Its zinc salt, $(C_3H_3O_3)_2Zn + 3H_2O$, is a crystalline powder, soluble with difficulty in water. All the salts are colored red by ferric chloride.

When the acid or its salts are heated with water, or if the acid be set free from its salts by mineral acids, it passes into a syrup-like, non-volatile mass.

Pyruvic acid forms crystalline compounds with the acid alkaline sulphites. It resembles the ketones in this respect. Nascent hydrogen (Zn and HCl, or HI) changes it to ordinary α-lactic acid, $CH_3.CH(OH).CO_2H$. PCl_5 converts it into the chloride of α-dichlorpropionic acid, $CH_3.CCl_2.COCl$ (p. 225). Pyroracemic acid, in aqueous, ethereal or acid solution, unites very readily with phenyl hydrazine to form $CH_3.C(HN_2.C_6H_5).CO_2H$, a crystalline solid, melting at 182° with decomposition (*Berichte*, 21, 987). This reaction will serve for the detection of minute quantities of the acid (*Berichte*, 16, 2242). With hydroxylamine it yields α-isonitrosopropionic acid (p. 224). It combines with CNH, like all ketone compounds, and forms an oxycyanide (p. 202), from which α-oxyisosuccinic acid is obtained. Pyruvic acid also condenses readily to benzene derivatives (p. 208). Thus, uvitic acid, $C_9H_8O_4$, results when the acid is heated with barium hydrate. Ammonia, however, produces uvitonic acid (by the decomposition of the imido-pyroracemic acid, which is first formed)—a pyridine derivative. It readily furnishes condensation products with hydrocarbons of the benzene series (*Berichte*, 14, 1595, and 16, 2071). It also unites with anilines and amido-acids (*Berichte*, 19, 2554).

It combines with bromine, forming a crystalline, unstable addition product, $C_3H_4O_3Br_2$. Substitution products result by heating the acid with bromine and water to 100°; *dibrom-pyruvic acid*, $CBr_2H.CO.CO_2H$, crystallizes with $2H_2O$ in large, rhombic plates. It loses its water of crystallization when exposed, and melts at 89°. *Tribrom-pyruvic acid*, $CBr_3.CO.CO_2H$ or $CBr_3.C(OH)_2.CO_2H$, is formed by heating α-lactic acid with bromine and water. It has two molecules of water of crystallization, and consists of brilliant leaflets which lose water at 100°, and then fuse at 90°. When heated with water or ammonia, it breaks up into bromoform, $CHBr_3$, and oxalic acid.

(2) **Propionyl-carboxylic Acid**, $C_2H_5.CO.CO_2H$, α-Ketobutyric Acid, is obtained from propionyl cyanide. It is very similar to pyruvic acid, and can only be distilled under diminished pressure. Nascent hydrogen converts it into α-oxybutyric acid.

(3) **Butyryl-carboxylic Acid**, $C_3H_7.CO.CO_2H$, is derived from butyryl cyanide, and boils at 180–185° with slight decomposition. It decomposes readily into CO_2 and butyric acid.

(4) **Trimethyl-Pyroracemic Acid**, $(CH_3)_3.C.CO.CO_2H$, results from the oxidation of pinacoline (p. 210) with potassium permanganate. It melts at 90° and boils at 185° (*Berichte*, 23, Ref. 21).

2. *β-Ketonic Acids.*

In the β-ketonic acids the ketone oxygen atom is attached to the second carbon atom, counting from the carboxyl group forward. These compounds are very unstable when free and when in the form of salts. Heat decomposes them into carbon dioxide and ketones. Their esters, on the other hand, are very stable, can be distilled without decomposition, and serve for various and innumerable syntheses.

The first acid of this class is:—

Aceto-acetic Acid, $C_4H_6O_3 = CH_3.CO.CH_2.CO_2H$, β-Keto-butyric Acid. We can regard this as acetic acid in which a hydrogen atom of methyl is replaced by acetyl, $CH_3.CO$, or as acetone, in which carboxyl has taken the place of a hydrogen atom—hence, the designation *acetone carboxylic acid.* To obtain the acid, the esters are saponified *in the cold* by dilute potash, or the barium salt is decomposed with sulphuric acid, and the solution shaken with ether (*Berichte*, **15**, 1781; **16**, 830). Concentrated over sulphuric acid, aceto-acetic acid is a thick liquid, strongly acid, and miscible with water. When heated, it yields carbon dioxide and acetone:—

$$CH_3.CO.CH_2.CO_2H = CH_3.CO.CH_3 + CO_2.$$

Nitrous acid converts it at once into CO_2 and isonitroso-acetone (p. 206). Its salts are not very stable. It is difficult to obtain them pure, and they sustain changes similar to those of the acid. Ferric chloride imparts to them, and also to the esters, a violet-red coloration. Occasionally the sodium or potassium salt is found in urine (*Berichte*, **16**, 2314).

The stable aceto-acetic esters, $CH_3.CO.CH_2.CO_2R$, are produced by the action of metallic sodium upon acetic esters. In this reaction the sodium compounds constitute the first product (Geuther, 1862; Frankland and Duppa):—

$$2\begin{array}{l}CH_3\\ |\\ CO.O.C_2H_5\end{array} + Na_2 = \begin{array}{l}CH_3\\ |\\ CO.CHNa.CO.O.C_2H_5\end{array} + C_2H_5.ONa + H_2.$$

By similar treatment acetic methyl ester yields the sodium compound of methyl aceto-acetic ester (see below). The free esters result upon treating their sodium compounds with acids. They are obtained pure by distillation. The aceto-acetic esters are liquids, dissolving with difficulty in water. They possess an ethereal odor. They can be distilled without decomposition. Like the free acid, they break up into carbon dioxide, acetone and alcohols, when heated with alkalies or acids:—

$$CH_3.CO.CH_2.CO_2R + H_2O = CH_3.CO.CH_3 + CO_2 + R.OH.$$

The formation of aceto-acetic ester is probably such that there first results a sodium aceto-acetic ester, $CH_2Na.CO_2.C_2H_5$, which in turn reacts with a second molecule of the acetic ester, a molecule of alcohol, separating at the same time (see *Berichte*, **18**, 3460):—

$$CH_3.CO_2.C_2H_5 + CH_2Na.CO_2.C_2H_5 = CH_3.CO.CHNa.CO_2.C_2H_5 + C_2H_5OH.$$

It may be, however, that an addition of sodium ethylate to aceto-acetic ester occurs (Claisen, *Berichte*, **20**, 651), and the additional product, $CH_3.C(OC_2H_8)_2.ONa$, reacts with a second molecule (Claisen, *Berichte*, **20**, 651; **21**, 1155).

Sodium also reacts analogously with propionic ester, forming propio-propionic ester (p. 342).

β-**Aldehydic esters** (p. 330) are formed if sodium, or sodium ethylate, acts upon a mixture of acetic ester (or the ester of any other monocarbonic acid) and formic ester, whereas, by using a mixture of ketones and formic esters, aldehyde ketones are produced. Diketones result if the mixture consists of ketones and acetic esters (p. 327). The oxalic esters and fatty acid esters yield keton-dicarboxylic acids (see oxalacetic acid). All these condensations, are analogous. An exit of alcohol occurs in each instance. They may well be termed *ester-condensations.* It is very probable that in every case the first action consists of the addition of sodium ethylate (*Berichte*, **21**, 1156; **22**, 553).

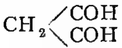
The esters of aceto-acetic acid, contrary to expectation, possess an *acid-like* character. They dissolve in alkalies, forming salt-like compounds in which a hydrogen atom is replaced by metals. All their reactions indicate that it is the hydrogen of the CH_2 (attached to two CO groups) that has the nature of an acid hydrogen.

We here observe an influence of the negative groups CO upon the hydrogen in union with carbon (in the atomic grouping $CO.CH_2.CO$) similar to that exercised by the nitro-group in the nitroparaffins (p. 107).

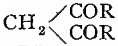
It matters not whether the carboxyl group be attached to hydrogen, forming the aldehyde or formyl group, or to an alkyl group, forming the ketone group, or to an oxyalkyl group, forming a carboxyl-ester group:—

—COH	—CO.R	—CO.OR
Aldehyde Group.	Ketone Group.	Carboxyl-ester Group.

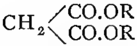
The union of two such groups to an atom of carbon gives rise to six classes of compounds:—


$CH_2{<}\begin{matrix}COH\\COH\end{matrix}$

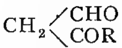
Dialdehydes.


$CH_2{<}\begin{matrix}COR\\COR\end{matrix}$

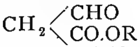
Diketones.


$CH_2{<}\begin{matrix}CO.OR\\CO.OR\end{matrix}$

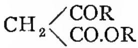
Dicarboxylic Esters.


$CH_2{<}\begin{matrix}CHO\\COR\end{matrix}$

Aldehyde Ketones.


$CH_2{<}\begin{matrix}CHO\\CO.OR\end{matrix}$

Aldehydic Acids.


$CH_2{<}\begin{matrix}COR\\CO.OR\end{matrix}$

Ketonic Acids.

These are acid in character. Their metallic derivatives are formed by the replacement of the hydrogen of the CH_2- (or CHR-) group.

The formyl group —CHO exercises the most powerful acid influence. Next in acidity is the ketone group —COR, while the ester group —CO.OR is the most feeble in its acid nature. Therefore, compounds containing the first group are the most acid. The β-diketones and the β-ketonic esters follow in regular succession. The entrance of an alkyl into the group CH_2 greatly diminishes the acid function of the homologous compounds (*Berichte*, **22**, 1018).

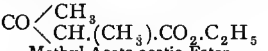
The sodium and potassium compounds are obtained pure from the aceto-acetic esters by treating the latter with potassium or sodium, or better, the alcoholates of the latter (in equivalent quantities):—

$$C_4H_5O_3.C_2H_5 + C_2H_5.ONa = C_4H_4NaO_3.C_2H_5 + C_2H_5.OH.$$

They dissolve readily in water and alcohol, react alkaline and on exposure decompose. The decomposition is more rapid on boiling with water (similar to the free aceto-acetic esters) (p. 334). Dilute acids liberate the esters. When the latter are dissolved in barium hydroxide, corresponding barium compounds are formed, from which derivatives of the heavy metals are obtained by double decomposition. Ammoniacal solutions of metallic salts afford the same directly from the aceto-esters (*Annalen*, **188**, 268). Consult *Annalen*, **201**, 143, upon the preparation of the dry sodium compounds.

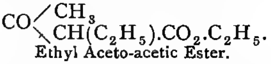
In quite a number of different reactions aceto-acetic ester conducts itself as if it possessed the constitution indicated by the formula of its isomeride β oxy-crotonic ester, $CH_3.C(OH):CH.CO_2.C_2H_5$. Hence many writers give the ester this constitution (Geuther, *Berichte*, 21, Ref. 295). The sodium salt is represented by the formula $CH_3.C(ONa):CH.CO_2.C_2H_5$ (A. Michael, *Berichte*, 21, Refs. 530 and 573). Usually the unsaturated hydroxylform, $C(OH):CH_2$, rearranges itself to the ketone form (p. 134). Yet, it appears, the reverse sometimes occurs (*Berichte*, 17, 2621). The two forms may therefore be considered pseudomeric or tautomeric (*Berichte*, 19, 730; 20, 651; 21, 1084).

Different monovalent radicals can be substituted for the metal in the sodium aceto-acetic esters. Thus by the action of the alkyl iodides (or bromides), sodium iodide separating, we get:—



$$CO\left\langle\begin{array}{l}CH_3\\ CH.(CH_3).CO_2.C_2H_5\end{array}\right.$$

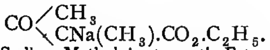
Methyl Aceto-acetic Ester.



$$CO\left\langle\begin{array}{l}CH_3\\ CH(C_2H_5).CO_2.C_2H_5.\end{array}\right.$$

Ethyl Aceto-acetic Ester.

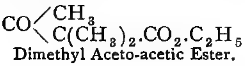
In these mono-alkylic aceto-acetic esters another hydrogen atom can be replaced by sodium, by the action of the metal or sodium ethylate:—



$$CO\left\langle\begin{array}{l}CH_3\\ CNa(CH_3).CO_2.C_2H_5.\end{array}\right.$$

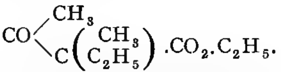
Sodium Methyl Aceto-acetic Ester.

If alkyl iodides be again permitted to act upon these last derivatives, a second alkyl group may be introduced, yielding dialkylic aceto-acetic esters, *e. g.*:—



$$CO\left\langle\begin{array}{l}CH_3\\ C(CH_3)_2.CO_2.C_2H_5\end{array}\right.$$

Dimethyl Aceto-acetic Ester.

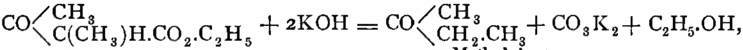


$$CO\left\langle\begin{array}{l}CH_3\\ C\left(\begin{array}{l}CH_3\\ C_2H_5\end{array}\right).CO_2.C_2H_5.\end{array}\right.$$

Methyl-ethyl Aceto-acetic Ester.

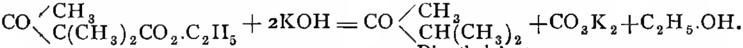
To execute these syntheses, it is not necessary to prepare pure sodium compounds. To the aceto-acetic ester dissolved in 10 times its volume of absolute alcohol, add an equivalent amount of sodium and then the alkyl iodide, after which heat is applied. To introduce a second alkyl, employ again an equivalent quantity of the sodium alcoholate and the alkyl iodide (*Annalen*, 192, 153). In some cases sodium hydroxide may be substituted for sodium ethylate in these syntheses (*Annalen*, 250, 123).

On heating the mono- or dialkylic aceto-acetic esters with alkalies in *dilute* aqueous or alcoholic solution, or with barium hydroxide, they decompose after the manner of aceto-acetic esters (p. 334), forming ketones (alkylic acetones) (*ketone decomposition*):—



$$CO\begin{matrix}CH_3\\ C(CH_3)H.CO_2.C_2H_5\end{matrix} + 2KOH = CO\begin{matrix}CH_3\\ CH_2.CH_3\end{matrix} + CO_3K_2 + C_2H_5.OH,$$

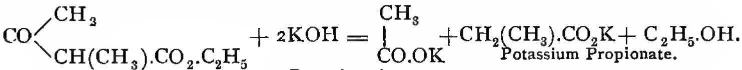
Methyl Acetone.



$$CO\begin{matrix}CH_3\\ C(CH_3)_2CO_2.C_2H_5\end{matrix} + 2KOH = CO\begin{matrix}CH_3\\ CH(CH_3)_2\end{matrix} + CO_3K_2 + C_2H_5.OH.$$

Dimethyl Acetone.

At the same time another splitting-off takes place, by which the alkylic acetic acids, *i. e.*, the higher fatty acids (p. 212) are produced along with acetic acid (*acid decomposition*):—



$$CO\begin{matrix}CH_3\\ CH(CH_3).CO_2.C_2H_5\end{matrix} + 2KOH = \begin{matrix}CH_3\\ |\\ CO.OK\end{matrix} + CH_2(CH_3).CO_2K + C_2H_5.OH.$$

Potassium Acetate. Potassium Propionate.

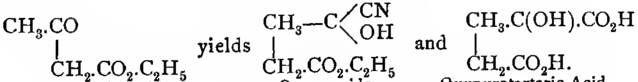
Both of these reactions, in which decomposition occurs (the splitting-off of ketone and of acid), usually take place simultaneously. In using dilute potash or caustic baryta, the ketone-decomposition predominates, whereas, with very concentrated alcoholic potash, the same may be asserted in regard to the acid-decomposition (J. Wislicenus, *Annalen*, 190, 276). The splitting-off of ketone, with elimination of CO_2, occurs almost exclusively on boiling with sulphuric or hydrochloric acid (1 part acid and 2 parts water). In this case, ketones, or with the dibasic ketonic acids, ketone monocarboxylic acids are produced (*Annalen*, 216, 133). The aceto-acetic esters undergo a decomposition similar to the splitting-off of acid if they are heated alone to 250°, or with sodium ethylate free from alcohol, when, instead of acetic acid, we obtain *dehydracetic acid*, $C_8H_8O_4$.

The aceto-acetic esters are changed by nascent hydrogen (sodium amalgam) into the corresponding β-oxy-acids (of the lactic acid series) (p. 331):—

$$CH_3.CO.CH_2.CO_2.C_2H_5 + H_2 + H_2O = CH_3.CH(OH).CH_2.CO_2H + C_2H_5.OH.$$

Aceto-acetic Ester. β-Oxybutyric Acid.

They are saponified at the same time. As ketones, they also unite with CNH, forming oxycyanides (p. 202), which hydrochloric acid converts into oxydicarboxylic acids:—



$$\begin{matrix}CH_3.CO\\ |\\ CH_2.CO_2.C_2H_5\end{matrix} \text{ yields } \begin{matrix}CH_3{-}C\begin{matrix}CN\\ OH\end{matrix}\\ |\\ CH_2.CO_2.C_2H_5\end{matrix} \text{ and } \begin{matrix}CH_3.C(OH).CO_2H\\ |\\ CH_2.CO_2H.\end{matrix}$$

Aceto-acetic Acid. Oxycyanide. Oxypyrotartaric Acid.

In the aceto-acetic esters, the hydrogen of the group $CO.CH_2.CO$ can be directly replaced by chlorine and bromine. The products, like

$CH_3.CO.CCl_2.CO_2.C_2H_5$ and $CH_3.CO.CCl(CH_3).CO_2.C_2H_5$,
Dichloraceto-acetic Ester. Chlormethylaceto-acetic Ester.

suffer changes with alkalies and acids analogous to those sustained by the aceto-acetic esters (see above). Thus, from dichloraceto-acetic esters are obtained dichloracetone, $CH_3.CO.CHCl_2$, and dichloracetic acid, $CHCl_2.CO_2H$; and from chlormethylaceto-acetic ester result chlormethyl-ethyl ketone, and α-chlorpropionic acid, $CH_3.CHCl.CO_2H$, etc.

All the aceto-acetic esters combine with hydroxylamine to form esters of the corresponding β-isonitroso-fatty acids (p. 214). Nitrous acid changes them to the isonitroso-derivatives, $CH_3.CO.C(N.OH).CO_2R$, which readily break up into isonitroso-acetone and CO_2 and alcohols (see below). The aceto-acetic esters with one alcohol radical decompose directly into isonitroso-acetones (p. 206).

The aceto-acetic esters combine with the diazo-compounds (*Berichte*, 21, 549) of the benzene series, and are capable of forming various condensation products (with aldehydes, etc.).

Ethyl Aceto-acetic Ester, $CH_3.CO.CH_2.CO_2.C_2H_5 = C_6H_{10}O_3$, *Aceto-acetic Ester*, is formed by the action of sodium upon ethyl acetic ester (p. 254). It also results when acetone-dicarbonic ester splits off a CO_2R-group. It is a pleasantly smelling liquid, of sp. gr. 1.0526 at 20°, boils at 180.8° and distils over with steam. The ester is only slightly soluble in water, and has a neutral reaction (that of the methyl ester is acid). Ferric chloride colors it violet.

Boiling alkalies or acids convert the ester into acetone, carbon dioxide and alcohol.

Preparation of Ethyl Aceto-acetic Ester.—60 parts metallic sodium are gradually dissolved in 2000 parts pure ethyl acetic ester. The excess of the latter is distilled off. On cooling the mass solidifies to a mixture of sodium aceto-acetic ester and sodium ethylate. The mass remaining liquid is mixed with acetic acid (50 per cent.) in slight excess. The oil separated and floating on the surface of the water is siphoned off, dehydrated with calcium chloride, and fractionated (*Annalen*, 186, 214 and 213, 137). For the preparation of the dry sodium compound, see *Annalen*, 201, 143.

The *sodium* compound, $C_4H_4NaO_3.C_2H_5$, crystallizes in long needles, and is made by heating ethyl acetic ester with sodium ethylate:—

$$2C_2H_3O_2.C_2H_5 + C_2H_5.ONa = C_6H_9NaO_3 + 2C_2H_5.OH.$$

The *copper salt*, $(C_6H_9O_3)_2Cu$, (Preparation, *Berichte*, 19, 21), is precipitated in the form of a bright green powder.

Heated alone or with sodium ethylate, it yields ethyl acetic ester and dehydracetic acid.

The pyron-group is then formed. The action of sulphuric acid causes aceto-acetic ester to pass into a condensation product, from which the isomeric iso-dehydracetic acid, $C_8H_8O_4$, splits off. Phosgene, $COCl_2$, and copper aceto-acetic ester yield dimethyl pyron-dicarboxylic ester (*Berichte*, 19, 22 and 20, 151).

Aceto-acetic ester becomes β-oxybutyric acid under the action of sodium amalgam. It forms an oxycyanide with CNH, from which oxypyrotartaric acid is formed (p. 337). PCl_5 replaces the oxygen of the CO-group by 2 atoms of chlorine. The *chloride*, $CH_3.CCl_2.CH_2.CO.Cl$, readily splits off hydrochloric acid and yields two chlor-crotonic acids (p. 239). Fuming nitric acid changes it to isonitroso-acetic ester (p. 222).

Chlorine (or sulphuryl chloride, SO_2Cl_2) and bromine convert aceto-acetic ester, or its copper derivative, into α-mono-, and di-substitution products. The CH_2-group is first attacked (*Berichte*, 21, Ref. 831; 22, Ref. 680; *Annalen*, 253, 168).

α-**Chlor-aceto-acetic Ester**, $CH_3.CO.CHCl.CO_2.C_2H_5$, is an oil with a very penetrating odor. It boils at 193°. In the action of chlorine, the γ-**chloraceto-acetic Ester**, $CH_2Cl.CO.CH_2.CO_2.C_2H_5$, is said to be produced simultaneously with the α-product. It boils at 188°. It yields citric acid with potassium cyanide (*Berichte*, 22, Ref. 255).

α-**Brom-aceto-acetic Ester**, $CH_3.CO.CHBr.CO_2.C_2H_5$, (see above), is an oil with piercing odor. It boils at 210°–215°. It attacks the eyes strongly.

α-**Dichloraceto-acetic Ester**, $CH_3.CO.CCl_2.CO_2.C_2H_5$, is a pungent-smelling liquid, boiling at 205°. Heated with HCl it decomposes into α-dichloracetone, $CH_3.CO.CHCl_2$, alcohol and CO_2; with alkalies it yields acetic and dichloracetic acids (*Berichte*, 16, 1553).

α-**Iodo aceto-acetic Ester**, $CH_3.CO.CHI.CO_2.C_2H_5$, is produced when iodine acts upon copper aceto-acetic ester. It is a green-colored oil. It forms a pyrazolon-derivative with phenylhydrazine (253, 194).

Isonitroso-aceto-acetic Ester, $CH_3.CO.C(N.OH).CO_2.C_2H_5$, is formed on dissolving ethyl aceto-acetate in dilute potash, adding a solution of potassium nitrite (1 molecule NO_2K) and acidifying with dilute sulphuric acid (*Berichte*, 15, 1326). Shining leaflets or prisms readily soluble in alcohol or ether; they melt at 53°, and decompose when heated (p. 338). It has an acid reaction, dissolves in alkalies with a yellow color and is colored an intense red by phenol and sulphuric acid (p. 107). Hydroxylamine forms di-iso nitroso-butyric ester, $CH_3.C(N.OH).C(N.OH).CO_2.C_2H_5$, with it (*Berichte*, 17, 821).

Ammonia converts aceto-acetic ester into paramido-aceto-acetic ester, $C_6H_{11}NO_2$, which may be regarded either as β **Imido-butyric Ester**, $CH_3.C(NH).CH_2.CO_2.C_2H_5$, or as β-**Amidocrotonic Ester**, $CH_3.C(NH_2):CH.CO.C_2H_5$ (*Annalen*, 226, 294). It crystallizes in bright leaflets, melts at 34°, and boils at 210°-215°, with partial decomposition. When distilled, it passes into a *lutidone* derivative (*Berichte*, 20, 445), while it forms hydrocollidine dicarboxylic ester with aldehyde.

Aceto-acetic ester also unites with methylamine and diethlyamine (*Berichte*, 18, 619). With aniline it yields phenyl-imido butyric acid (see this), which easily passes over into quinoline derivatives. With amidines, pyrimidine compounds result (*Berichte*, 18, 759). Acetamide and aceto-acetic ester form aceto-β-imido-butyric ester (*Berichte*, 18, Ref. 141). Pyrazolon-derivatives are formed by union with phenylhydrazine (see these).

Nitrous acid converts β-imidobutyric ester into *imido-isonitroso-butyric ester*, $CH_3.C(NH).C(N.OH).CO_2.C_2H_5$. This is a yellow oil. When reduced with zinc dust, it condenses to dimethyl-pyrrol-dicarboxylic ester (*Berichte*, 17, 1638). Zinc chloride condenses it to a *ketine* derivative (see Ketines).

Methyl Aceto-acetic Ester, $CH_3.CO.CH_2.CO_2.CH_3$, is formed from methyl acetate (p. 338). It boils at 170°, and is colored a dark cherry-red by ferric chloride. Otherwise it is perfectly similar to the ethyl ester.

Methyl Ethyl Aceto-acetic Ester, $CO\Big\langle\begin{array}{l}CH_3\\C(CH_3)H.CO_2.C_2H_5\end{array}$ $= C_7H_{12}O_3$ (p. 336), (α-aceto-propionic ester). This boils at 186° and has a specific gravity of 1.01 at 12°. Potash readily decomposes it into methyl acetone, carbon dioxide and alcohol. By the acid-decomposition it yields propionic acid. *Free* methyl aceto-acetic acid, obtained by saponification of the ester with alkalies in the cold, is very similar to aceto-acetic acid (p. 336).

Dimethyl Aceto-acetic Ester, $CO\Big\langle\begin{array}{l}CH_3\\C(CH_3)_2.CO_2.C_2H_5\end{array} = C_8H_{14}O_3$, is an oil, nearly insoluble in water, of sp. gravity 0.991 at 16°. It boils at 190°. Boiling aqueous potash does not affect it. Alcoholic potash, however, or baryta water, changes it to dimethyl acetone, carbon dioxide, and alcohol. By the acid-decomposition it yields isobutyric acid, $(CH_3)_2.CH.CO_2H$. The *free* acid is crystalline, but very unstable.

Ethyl Aceto-acetic Ester, $CO\Big\langle\begin{array}{l}CH_3\\CH(C_2H_5).CO_2.C_2H_5\end{array}$, is sparingly soluble in water. It boils at 195°. Its specific gravity equals 0.998 at 6°. Ferric chloride colors it blue. Boiled with aqueous potash, it decomposes into ethylacetone, carbon dioxide, and alcohol. In the acid-decomposition it forms normal butyric acid.

Diethyl Aceto-acetic Ester, $CO\Big\langle\begin{array}{l}CH_3\\C(C_2H_5)_2.CO_2.C_2H_5\end{array} = C_{10}H_{18}O_3$, is insoluble in water, boils at 210–212°, and has a specific gravity at 0° of 0.974. Aqueous potash has no effect upon it, while with alcoholic potash or baryta water it yields diethyl ketone, $CH_3.CO.CH(C_2H_5)_2$. By the acid-decomposition (with sodium ethylate) diethylacetic acid results. The free diethyl-aceto-acetic acid is liquid, and when distilled, yields CO_2 and diethyl acetone.

Methyl-ethyl Aceto-acetic Ester, $CO\Big\langle\begin{array}{l}CH_3\\C(CH_3)(C_2H_5).CO_2.C_2H_5\end{array} = C_9H_{18}O_3$, boils at 198°. By decomposition it furnishes methyl-ethyl acetone and methyl-ethyl acetic acid (p. 229).

For other mixed alkyl aceto-acetic esters consult *Annalen*, 226, 206.

Allyl Aceto-acetic Ester, $CO\Big\langle\begin{array}{l}CH_3\\CH(C_3H_5).CO_2.C_2H_5\end{array} = C_9H_{14}O_3$, is obtained by the action of allyl iodide upon sodium aceto-acetic ester. It boils at 206°; its specific gravity is 0.982 at 17.5°. Ferric chloride gives a carmine-red coloration. When it decomposes, allyl acetone and allyl acetic acid are produced (p. 241). Sodium amalgam changes it into allyloxybutyric acid. By the addition of more allyl, we obtain—

Diallyl aceto-acetic Ester, $CO\Big\langle\begin{array}{l}CH_3\\C(C_3H_5)_2.CO_2.C_2H_5\end{array}$, which boils at 206°, and decomposes into diallyl acetone and diallyl acetic acid.

By the action of propyl iodide, isopropyl iodide, isobutyl iodide, amyl iodide, benzyl chloride, $C_6H_5.CH_2Cl$, etc., higher aceto-acetic esters have been formed, from which, by decomposition, higher ketones and fatty acids resulted, and were converted into higher oxy-acids by the addition of H_2.

The following is an α-γ-ketonic ester:—

Acetonyl-aceto-acetic Ester, $CH_3.CO.CH_2.CH\Big\langle\begin{array}{l}CO.CH_3\\CO_2.C_2H_5\end{array}$, is produced by the action of chloracetone, $CH_3.CO.CH_2Cl$, upon aceto-acetic ester. It forms pyrotritaric ester (*Berichte*, 17, 2759) with fuming hydrochloric acid. On heating the ester with water to 160° C. acetonyl acetone results.

By the action of chlorcyanogen upon sodium methyl aceto-acetic ester the following derivatives are produced:—

Methyl Cyan-acetoacetic Ester, $CH_3.CO.CH(CN).CO_2.CH_3$. This can be prepared from methyl cyanacetic ester when acetyl chloride acts upon its sodium compound (*Berichte*, 21, Ref. 187; 22, Ref. 207). It is crystalline, readily soluble in alcohol and ether, and melts at 46°. Its reaction is acid. Its salts crystallize well.

Ethyl Cyan-acetoacetic Ester, $CH_3.CO.CH(CN).CO_2.C_2H_5$, from ethyl cyanacetic ester, melts at 26°.

Methyl and ethylaceto-acetic esters yield corresponding cyanogen products, $CH_3.CO.C(CN)R.CO_2.C_2H_5$. These are insoluble in alkalies (*Berichte*, 22, Ref. 407).

The hydrogen in the aceto-acetic esters may also be replaced by *acid radicals*, by letting the acid chlorides act on the sodium compounds, suspended in ether. Thus arise the *diketon-monocarboxylic esters.* Acetyl chloride forms:—

Acetyl Aceto-acetic Ester, $C_2H_3O.CH(C_2H_3O).CO_2.C_2H_5$ or **Diaceto-acetic Ester,** $\left.\begin{matrix}CH_3.CO\\CH_3.CO\end{matrix}\right>CH.CO_2.C_2H_5$. It boils with partial decomposition at 210°, and is broken up by water, even at ordinary temperatures, into acetic acid, aceto-acetic ester and CO_2 (*Annalen*, 226, 210). Sodium ethylate displaces an acetyl group in it, forming aceto-acetic ester and sodium aceto-acetic ester: $\left.\begin{matrix}C_2H_3O\\C_2H_3O\end{matrix}\right>CH.CO_2.C_2H_5 + C_2H_5.ONa = C_2H_3O.CHNa.CO_2.C_2H_5 + C_2H_3O.O.C_2H_5$. Acetyl-methyl-aceto-acetic ester and acetyl-ethyl-aceto-acetic ester, $(C_2H_3O)_2C(C_2H_5).CO_2.C_2H_5$, are produced in an analogous manner.

Benzoyl aceto-acetic Ester, $\left.\begin{matrix}CH_3.CO\\C_6H_5.CO\end{matrix}\right>CH.CO_2.C_2H_5$, obtained from aceto-acetic ester by benzoyl chloride, breaks up, when boiled with sulphuric acid, into benzoyl acetone, $CH_3.CO.CH_2.CO.C_6H_5$ (*Berichte*, 16, 2239), and CO_2.

The following is a monobasic *Diketonic Acid*:—

Aceto-pyroracemic Acid, $C_5H_6O_4 = CH_3.CO.CH_2.CO.CO_2H$, or **Acetone Oxalic Acid.** Its ethyl ester results when sodium ethylate acts upon acetone and oxalic ester. It boils at 214° (*Berichte*, 20, 2189). Ferric chloride imparts a dark red color to it. Copper acetate precipitates the green copper compound $(C_6H_5O_4)_2$ from its alcoholic solution. The acid, liberated from the ester, condenses quite readily to symmetrical oxytoluic acid (*Berichte*, 22, 3271). As a β-diketone compound $(CO.CH_2.CO)$, acetone-oxalic ester manifests all the reactions peculiar to this class.

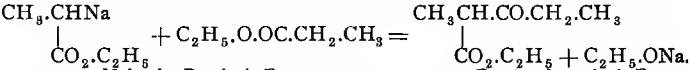
Acetophenone, $C_6H_5.CO.CH_3$, by treatment analogous to that just described above, passes into the ester of benzoyl pyroracemic acid, $C_6H_5.CO.CH_2.CO.CO_2H$ (see this).

Acid residues can also be introduced into the aceto-acetic esters, by allowing esters of substituted fatty acids to act upon the sodium compounds. The esters of the ketone dicarboxylic acids are obtained in this way. Chlorformic ester produces

Aceto-malonic Ester, $CH_3.CO.CH\left\langle\begin{array}{l}CO_2.C_2H_5\\CO_2.C_2H_5\end{array}\right.$. Chloracetic ester, $CH_2Cl.CO_2.R$, yields

Aceto-succinic Ester, $CH_3.CO.CH\left\langle\begin{array}{l}CH_2.CO_2.R\\CO_2.R\end{array}\right.$. These dibasic ketonic acids will be discussed after the oxy-acids. **Diacetyl succinic Ester,** $\begin{array}{l}CH_3.CO.CH.CO_2.C_2H_5\\ \quad\quad\quad\;|\\CH_3.CO.CH.CO_2.C_2H_5\end{array}$, a rather remarkable body, produced by the action of iodine upon sodium aceto-acetic ester, properly belongs in the same section.

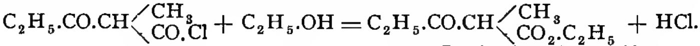
Sodium also facilitates the conversion of propionic ester into α-propionyl-propionic ester (*Berichte*, 20, 1320 and *Annalen* 239, 386):—



$$\begin{array}{l}CH_3.CHNa\\ \quad|\\ \quad CO_2.C_2H_5\end{array} + C_2H_5.O.OC.CH_2.CH_3 = \begin{array}{l}CH_3CH.CO.CH_2.CH_3\\ \quad|\\ \quad CO_2.C_2H_5\end{array} + C_2H_5.ONa.$$

2 Molecules Propionic Ester. α-Propionyl-propionic Ester.

On the other hand normal butyric ester, isobutyric ester and isovaleric ester, when acted upon by sodium, do not yield analogous compounds, but the oxy-alkyl derivatives of higher fat-acids (*Berichte*, 22, Ref. 22). The action of ferric chloride upon fatty acid chlorides is a common synthetic method for the preparation of higher β-ketonic acid esters. In this reaction the chlorides of the ketones are first formed: $2C_2H_5.CO.Cl = C_2H_5.CO.CH\left\langle\begin{array}{l}CH_3\\CO.Cl\end{array}\right. + HCl$. When treated with water they split off CO_2, and become ketones (p. 200). With alcohol they are converted into esters of the ketonic acids (Hamonet, *Berichte*, 22, Ref. 766):—



$$C_2H_5.CO.CH\left\langle\begin{array}{l}CH_3\\CO.Cl\end{array}\right. + C_2H_5.OH = C_2H_5.CO.CH\left\langle\begin{array}{l}CH_3\\CO_2.C_2H_5\end{array}\right. + HCl.$$

α-Propionyl-propionic Acid.

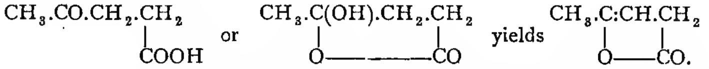
α-**Propionyl-propionic Ester,** $C_2H_5.CO.CH\left\langle\begin{array}{l}CH_3\\CO_2.C_2H_5\end{array}\right.$, prepared by both methods, is an agreeably smelling liquid, boiling at 199°; its specific gravity at 0° is 0.995. Sodium alcoholate and ethyl iodide do not convert it into ethyl propionyl-propionic ester, but into the decomposition products of the latter—propionic ester and methyl ethyl acetic ester. Sodium amalgam converts it into the corresponding oxy-acid, which passes into methyl propyl acetic acid by reduction (p. 230).

Succinyl–succinic Ester, $C_{12}H_{16}O_6 = \begin{array}{l}\quad\quad\quad CH_2.CO.CH.CO_2.C_2H_5\\ \quad\quad\quad\;|\quad\quad\quad\;|\\C_2H_5.CO_2.CH.\;\;CO.CH_2\end{array}$, may be similarly obtained from succinic ethyl ester by the action of sodium or sodium alcoholate. This new compound is doubtless a quino-tetrahydro-dicarboxylic ester, and will be considered under the benzene derivatives.

3. *γ-Ketonic Acids.*

These have the ketone oxygen atom attached to the third carbon atom from the carboxyl group (p. 331) and are distinguished from the acids of the *β*-variety by the fact that they are stable in a free condition even when heated. By the addition of two hydrogen atoms they yield *γ*-oxy-acids, which immediately pass into lactones (see these).

When distilled, the *γ*-ketonic acids split off water and pass into unsaturated lactones (*Berichte*, **18**, 2263). This transposition may be explained by assuming that the tautomeric form of the *γ*-lactone is to be ascribed to the *γ*-ketone acids (*Annalen*, **226**, 225):—



$$\begin{array}{c}CH_3.CO.CH_2.CH_2\\ |\\ COOH\end{array} \text{ or } \begin{array}{c}CH_3.C(OH).CH_2.CH_2\\ |\qquad\qquad |\\ O\text{———————}CO\end{array} \text{ yields } \begin{array}{c}CH_3.C{:}CH.CH_2\\ |\quad |\\ O\text{——}CO.\end{array}$$

Lævulinic Acid. Angelica Acetone.

β-Aceto-propionic Acid, $C_5H_8O_3 = CH_3.CO.CH_2.CH_2.CO_2H$, **Lævulinic Acid**, *γ*-Ketovaleric Acid. This is isomeric with methyl aceto-acetic acid, which may be designated *α*-aceto-propionic acid (p. 340). It is obtained from aceto-succinic ester (p. 342) on boiling with hydrochloric acid or baryta water, and from cane sugar, lævulose, starch, and apparently from all the carbohydrates (*Berichte*, **19**, 707) on boiling them with dilute hydrochloric or sulphuric acid.

Preparation.—Heat 500 grs. of sugar dissolved in 1 litre of water with 250 grs. of crude concentrated hydrochloric acid until the separation of brown humus substances ceases. The solution is then concentrated, repeatedly extracted with ether, and the lævulinic acid, remaining after the evaporation of the ethereal solution, is purified by distillation in a vacuum. A yield of about 8 per cent. of acid is obtained in this way (*Annalen*, **227**, 99).

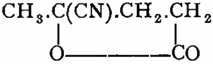
A more advantageous method is to boil starch with hydrochloric acid (*Berichte*, **20**, 1775). The yield of acid is about 13 per cent. It is obtained commercially by heating cane sugar with dilute hydrochloric acid (*Berichte*, **19**, 2572).

Lævulinic acid dissolves very readily in water, alcohol and ether, and crystallizes in scales, melting at 33.5°. The acid boils with slight decomposition at 239°. Traces of moisture lower the melting point. The molecular refractions of the free acid and its esters confirm the idea of its being a ketonic acid (p. 60).

In accordance with this view it yields *γ*-isonitrosovaleric acid (p. 228) with hydroxylamine. It unites with phenylhydrazine acetate to form phenylhydrazine-lævulinic acid, $C_6H_5.N_2H{:}C(CH_3).CH_2.CH_2.CO_2H$. This passes into an anhydride, $C_{11}H_{12}N_2O$, when heated to 166° (*Berichte*, **22**, Ref. 673). It melts at 108°. The hydrazone yields *γ*-amidovaleric acid by reduction (p. 319).

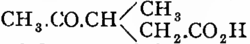
The *calcium salt*, $(C_5H_7O_3)_2Ca + 2H_2O$, forms delicate needles; the *barium salt* is a gummy mass. The *silver salt* is a characteristic, crystalline precipitate, dissolving in water with difficulty. The *methyl ester*, $C_5H_7(CH_3)O_3$, boils at 191°, the *ethyl ester* at 200°.

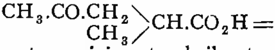
When heated to 150–200° with hydriodic acid and phosphorus, lævulinic acid is changed to normal valeric acid. By the action of sodium amalgam sodium γ-oxyvalerate is produced. The acid liberated from this becomes valerolactone. Dilute nitric acid converts lævulinic acid (analogous to the oxidation of ketones, p. 203) into acetic and malonic acid and again into succinic acid and carbon dioxide.

Lævulinic acid unites with potassium cyanide, forming the *lactone cyanide*,  , from which α-methyl-glutaric acid is obtained by hydrochloric acid (*Berichte*, **19**, 3269).

Two *angelica lactones*, $C_5H_6O_2$ (α and β), are produced on distilling lævulinic acid. Water separates at the same time. The α-derivative yields β-bromlævulinic acid by the addition of hydrobromic acid.

β-Bromlævulinic Acid, $CH_3.CO.CHBr.CH_2.CO_2H$, obtained from the lactone (see above), melts at 59°. Its *ethyl ester* is produced in the bromination of lævulinic ester, and boils at 240°. It yields diaceto-glutaric ester (*Berichte*, **19**, 47) with sodacetoacetic ester. Warming with sodium hydroxide converts the β-bromlævulinic acid into hydroxy-lævulinic acid and aceto-acrylic acid (see below) (*Berichte*, **20**, 425). Aniline converts brom-lævulinic acid into dimethyl-indol, as all compounds with the group —CO.CHBr— react analogously (*Berichte*, **21**, 3360).

β-Aceto-butyric Acid,  $CH_3.CO.CH\left\langle\begin{matrix}CH_3\\CH_2.CO_2H\end{matrix}\right. = C_6H_{10}O_3$, β-methyl aceto-propionic acid, is obtained from α-methyl aceto-succinic ester (p. 342). It boils at 242° and becomes crystalline at —12°. The ethyl ester boils near 205°. The isomeric—

β-Aceto-isobutyric acid,  $\left.\begin{matrix}CH_3.CO.CH_2\\CH_3\end{matrix}\right\rangle CH.CO_2H = C_6H_{10}O_3$, α-methyl-lævulinic acid, from β-methyl aceto-succinic ester, boils at 248°. Its ethyl ester boils at 207°.

Nitric acid oxidizes both acids to CO_2 and methyl succinic acid (pyrotartaric acid). Consult *Berichte*, **23**, 622 upon the lactone formation of the alkyl-lævulinic acids.

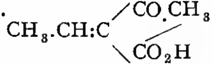
δ-Ketonic Acid.

γ-Aceto-butyric Acid, $CH_3.CO.CH_2.CH_2.CH_2.CO_2H = C_6H_{10}O_3$, is obtained from the ester of aceto-glutaric acid (p. 341) by the withdrawal of CO_2. It melts at 13° and boils at 275°. Sodium amalgam converts it into a salt of δ-oxycaproic acid, which yields a δ-lactone (*Annalen*, **216**, 127).

UNSATURATED KETONIC ACIDS.

β-Aceto-acrylic Acid, $CH_3.CO.CH:CH.CO_2H$, is derived from β-bromlævulinic acid (see above) upon digestion with a soda solution. It crystallizes from alcohol in brilliant needles melting at 125° C. It combines with phenylhydrazine (*Berichte*, **21**, 2937) and with bromine, forming in the latter case dibrom-lævulinic acid. Ammonia converts this into tetramethyl pyrazine (dimethyl ketine) (*Berichte*, **20**, 426).

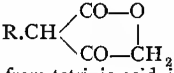
β-Trichlor-aceto-acrylic Acid, $CCl_3.CO.CH:CH.CO_2H$, is very probably *Trichlorphenomalic Acid.* This is obtained from benzene by the action of potassium chlorate and sulphuric acid (*Annalen*, **223**, 170). It crystallizes from water in shining leaflets, melting at 131°. It breaks up into chloroform and maleïc acid when boiled with barium hydroxide.

Ethidene Aceto-acetic Acid, 
$$CH_3.CH:C\begin{cases}CO.CH_3\\CO_2H\end{cases}$$
. The ethyl ester results from the action of hydrochloric acid upon aldehyde and aceto-acetic ester. A liquid with penetrating odor, and boiling at 211°. Caustic potash decomposes it (*Annalen*, **218**, 172).

A series of homologous acids, $C_nH_{2n-4}O_3$, has been prepared from the brominated alkyl aceto-acetic esters by the action of alcoholic potash, or by heating them alone or with water. These have been called pentinic, tetrinic acids, etc., etc. (Demarcay).

Tetrinic Acid melts at 189° and boils at 262°. It takes on a violet color upon the addition of ferric chloride.

Pentinic Acid melts at 126.5° and is colored cherry-red by ferric chloride.

The two compounds appear, however, not to be carboxylic acids, but are more properly *ketolactones* of the formula 
$$R.CH\begin{cases}CO-O\\ \quad\;\;|\\CO-CH_2\end{cases}$$
(see *Berichte*, **21**, 2603; **22**, 243).

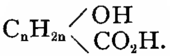
The *Oxy-tetrinic Acid*, $C_5H_6O_4$, from tetrinic acid, is identical with mesaconic acid (*Berichte*, **21**, Ref. 180).

The *sulpho-carboxylic acids* are analogues of the keton-carboxylic acids. They form α-, β-, and γ-derivatives:—

$C_6H_5.SO_2.CO_2H$	$C_2H_5.SO_2.CH_2.CO_2H$	$C_2H_5.SO_2.CH_2.CH_2.CO_2H$.
Phenyl sulpho-formic Acid.	Ethyl sulpho-acetic Acid.	Ethyl sulpho-propionic Acid.

These are prepared by the action of the sulphinates, $R.SO_2Na$, upon the esters of chlorfatty acids, *e. g.*, chlorformic ester, $ClCO_2R$, chloracetic ester, etc. (*Berichte*, **21**, 89, 992).

ALCOHOL- OR OXY-ACIDS.


$$C_nH_{2n}\begin{cases}OH\\CO_2H.\end{cases}$$

Acids of this series, with the empirical formula, $C_nH_{2n}O_3$, show a twofold character in their entire deportment. Since they contain a carboxylic group, they are *monobasic acids* with all the attaching properties and transpositions of the latter; the OH-group linked to the radical bestows upon them all the properties of the *monohydric alcohols*. They may, therefore, be designated *alcohol acids* (corresponding to the ketonic acids, p. 331, and the aldehyde acids, p. 329). They were formerly called *divalent or dihydric* (*diatomic*) *acids*, as they contained two hydroxyl groups (an alcoholic and an acid) and could be obtained by oxidizing the dihydric alcohols (p. 297). At present they are mostly termed *oxy-* or *hydroxy-fatty* *acids*, because of their origin from the fatty-acids by the replacement of a hydrogen atom by OH :—

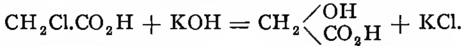
$$C_2H_5.CO_2H \quad \text{and} \quad C_2H_4\left\langle\begin{matrix}OH\\CO_2H\end{matrix}\right. .$$

Propionic Acid. Oxypropionic Acid.

This view of them is especially well adapted for the nomenclature of the acids (p. 348).

The following are the chief methods of producing the oxy-acids :—

1. The transposition of the mono-halogen fatty acids with silver oxide, boiling alkalies, or even water :—



$$CH_2Cl.CO_2H + KOH = CH_2\left\langle\begin{matrix}OH\\CO_2H\end{matrix}\right. + KCl.$$

Monochloracetic Acid. Oxy-acetic Acid.

The conditions of the reaction are perfectly similar to those observed in the conversion of the alkylogens into alcohols (p. 119). The α-derivatives yield α-oxy-acids; the β-derivatives are occasionally changed to unsaturated acids by the splitting-off of a haloid acid (p. 235), while the γ-compounds form γ-oxy-acids, which subsequently pass into lactones. γ-Halogen acids are converted directly into lactones by the alkaline carbonates.

The oxy-acids can be reconverted into fatty acids by heating them with hydriodic acid (p. 94) :—

$$CH_2(OH).CO_2H + 2HI = CH_3.CO_2H + H_2O + I_2,$$

or are first changed to monobrom-acids with hydrobromic acid :—

$$CH_2(OH).CO_2H + HBr = CH_2Br.CO_2H + H_2O,$$

and the product reduced with nascent hydrogen.

2. Some fatty acids have OH directly introduced into them. This is accomplished by oxidizing them with $KMnO_4$ in alkaline solution :—

$$(CH_3)_2.CH.CO_2H + O = (CH_3)_2.C(OH)CO_2H.$$

Isobutyric Acid. α-Oxyisobutyric Acid.

Only acids containing the tertiary group CH (a so-called tertiary H-atom) are adapted to this kind of transposition (*Annalen*, 208, 60, 220, 56). Nitric acid effects the same as MnO_4K (*Berichte*, 14, 1782; 15, 2318).

3. The action of nascent hydrogen (sodium amalgam, zinc and hydrochloric acid) upon the ketonic acids and their esters (p. 331):—

$$CH_3.CO.CO_2H + H_2 = CH_3.CH(OH).CO_2H.$$

Racemic Acid. α-Oxypropionic Acid.

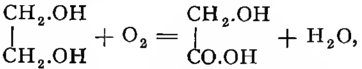
4. By the action of nitrous acid upon amido-acids :—

$$CH_3(NH_2).CO_2H + NO_2H = CH_2(OH).CO_2H + N_2 + H_2O.$$

Amido-Acetic Acid. Oxyacetic Acid.

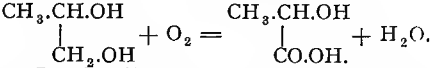
This reaction is perfectly similar to that observed in the conversion of amines into alcohols (p. 161). The intermediate products are the diazofatty acids, and on boiling them with water or dilute acids oxyacids result (see these).

5. Careful oxidation of the glycols with dilute nitric acid or platinum sponge:—



$$\begin{array}{l}CH_2.OH\\ |\\ CH_2.OH\end{array} + O_2 = \begin{array}{l}CH_2.OH\\ |\\ CO.OH\end{array} + H_2O,$$

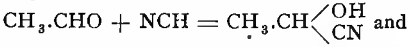
Glycol. Glycollic Acid.



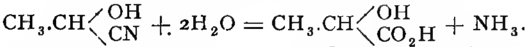
$$\begin{array}{l}CH_3.CH.OH\\ \quad|\\ CH_2.OH\end{array} + O_2 = \begin{array}{l}CH_3.CH.OH\\ \quad|\\ CO.OH.\end{array} + H_2O.$$

a-Propylene Glycol. a-Lactic Acid.

6. By allowing hydrocyanic acid and hydrochloric acid to act upon the aldehydes and ketones. At first oxycyanides are produced (p. 202), after which hydrochloric acid changes the cyanogen group into carboxyl:—



$$CH_3.CHO + NCH = CH_3.CH\begin{array}{l}\diagup OH\\ \diagdown CN\end{array} \text{ and}$$



$$CH_3.CH\begin{array}{l}\diagup OH\\ \diagdown CN\end{array} + 2H_2O = CH_3.CH\begin{array}{l}\diagup OH\\ \diagdown CO_2H\end{array} + NH_3.$$

a-Oxypropionic Acid.

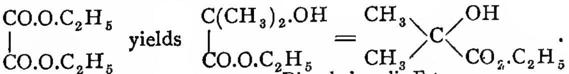
In preparing the oxycyanides, the aldehydes or ketones are heated under pressure, with the equivalent amount of hydrocyanic acid (from 20–30 per cent.). Or we can add pulverized potassium cyanide to the ethereal solution of the ketone, and follow it with the gradual addition of concentrated hydrochloric acid (*Berichte*, 14, 1965; 15, 2318). The concentrated hydrochloric acid changes the cyanides to acids, the amides of the acids being at first formed in the cold, but on boiling with more dilute acid they sustain further change to acids. Sometimes the change occurs more readily by heating with a little dilute sulphuric acid.

The glycol chlorhydrins (p. 302) undergo a like alteration through the action of potassium cyanide and acids:—

$$CH_2.(OH).CH_2Cl + CNK = CH_2(OH).CH_2.CN + KCl \text{ and}$$
$$CH_2.(OH).CH_2CN + 2H_2O = CH_2(OH).CH_2.CO_2H + NH_3.$$

β-Oxypropionic Acid.

7. A method of ready applicability in the synthesis of oxyacids consists in permitting zinc and alkyl iodides to act upon diethyl oxalic ester (Frankland and Duppa). This reaction is like that in the formation of tertiary alcohols from the acid chlorides by means of zinc ethyl, or of the secondary alcohols from formic esters (p. 121)—1 and 2 alkyl groups are introduced into one carboxyl group (*Annalen*, 185, 184):—

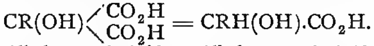


Oxalic Ester. Dimethyl-oxalic Ester.

If we employ two alkyl iodides two different alkyls may be introduced.

The acids obtained, as indicated, are named in accordance with their derivation from oxalic acid, but it would be more correct to view them as derivatives of oxy-acetic acid or glycollic acid, $CH_2(OH).CO_2H$, and designate, *e. g.*, dimethyl-oxalic acid, as dimethyl-oxyacetic acid.

8. The fatty acids are formed from alkyl malonic acids, $CRR'(CO_2H)_2$, by the withdrawal of one carboxyl group (p. 212), and the oxy-fatty acids are obtained in a similar manner from alkyl oxymalonic acids or tartronic acids:—



$$\mathrm{CR(OH)}\left\langle\begin{matrix}\mathrm{CO_2H}\\ \mathrm{CO_2H}\end{matrix}\right. = \mathrm{CRH(OH).CO_2H.}$$

Alkyl-tartronic Acid. Alkyl-oxy-acetic Acid.

The tartronic compounds are synthetically prepared from malonic acid esters, *e. g.*, $\mathrm{CH_2}\left\langle\begin{matrix}\mathrm{CO_2.C_2H_5}\\ \mathrm{CO_2.C_2H_5}\end{matrix}\right.$, by first introducing the alkyl group (see malonic acid), then replacing the second hydrogen of CH_2 by chlorine, and finally saponifying the alkylic monochlor-malonic ester with baryta (*Berichte*, 14, 619). The successive transformations correspond to the formulas:—

$$\mathrm{CH_2}\left\langle\begin{matrix}\mathrm{CO_2.CH_3}\\ \mathrm{CO_2.CH_3}\end{matrix}\right. \quad \mathrm{CHR}\left\langle\begin{matrix}\mathrm{CO_2.CH_3}\\ \mathrm{CO_2.CH_3}\end{matrix}\right. \quad \mathrm{CRCl}\left\langle\begin{matrix}\mathrm{CO_2.CH_3}\\ \mathrm{CO_2.CH_3}\end{matrix}\right. \text{ and } \mathrm{CR(OH)}\left\langle\begin{matrix}\mathrm{CO_2H}\\ \mathrm{CO_2H}\end{matrix}\right..$$

The possible isomerides of the dihydric acids are best derived from their corresponding monobasic acids, by replacing a hydrogen atom in the latter by OH.

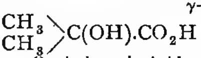
Only one oxy-acid can be derived from acetic acid, viz., glycollic acid, $CH_2.OH.COOH$. From propionic acid, $CH_3.CH_2.CO_2H$, we can obtain two oxy-acids. Five isomerides agree with the formula, $\mathrm{C_4H_8O_3} = \mathrm{C_3H_6}\left\langle\begin{matrix}\mathrm{OH}\\ \mathrm{CO_2H}\end{matrix}\right.$; three of them are derived from normal butyric acid, $CH_3.CH_2.CH_2.CO_2.H$, and two from isobutyric acid, $(CH_3)_2CH.CO_2H$, etc.

The above compounds are named like the substituted fatty acids (p. 223), *i. e.*, as α-, β-, -γ, etc., oxy-acids:—

$CH_3.CH(OH).CO_2H$
α-Oxypropionic Acid.

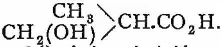
$CH_2(OH).CH_2.CO_2H$
β-Oxypropionic Acid.

$CH_2(OH).CH_2.CH_2.CO_2H$
γ-Oxybutyric Acid.



$$\begin{matrix}\mathrm{CH_3}\\ \mathrm{CH_3}\end{matrix}\Big\rangle\mathrm{C(OH).CO_2H}$$

α-Oxyisobutyric Acid.



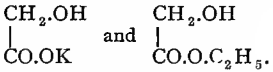
$$\begin{matrix}\mathrm{CH_3}\\ \mathrm{CH_2(OH)}\end{matrix}\Big\rangle\mathrm{CH.CO_2H.}$$

β-Oxyisobutyric Acid.

The α- and β-oxy-acids exist free, while the γ-acids are only known in their salts and acids. When liberated from the latter they immediately give up a molecule of water and pass into their anhydrides, the lactones. Various other peculiarities distinguish them (p. 350).

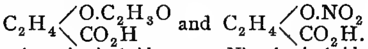
The oxy-fatty acids containing one OH group are, in consequence, more readily soluble in water, and less soluble in ether than the parent acids (p. 297). They are less volatile, and as a general thing, cannot be distilled without undergoing a change.

Their chemical properties fully accord with their structure, by which they are both acids and alcohols. The acid hydrogen (of the carboxyl group) can be easily replaced by metals and hydrocarbon residues, thus giving rise to normal salts and esters:—



$$\begin{array}{l}CH_2.OH\\ |\\ CO.OK\end{array} \quad \text{and} \quad \begin{array}{l}CH_2.OH\\ |\\ CO.O.C_2H_5.\end{array}$$

The remaining OH-group deports itself like that of the alcohols. Alkali metals and alkyls may replace its hydrogen. Acid radicals and NO_2 are substituted for it by the action of chlorides of monobasic acid radicals (like $C_2H_3O.Cl$), and a mixture of concentrated nitric and sulphuric acids:—

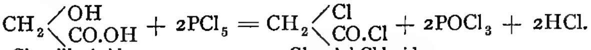


$$C_2H_4\left\langle\begin{array}{l}O.C_2H_3O\\CO_2H\end{array}\right. \quad \text{and} \quad C_2H_4\left\langle\begin{array}{l}O.NO_2\\CO_2H.\end{array}\right.$$

Aceto-lactic Acid. Nitro-lactic Acid.

Both these reactions are characteristic of the hydroxyl groups of the alcohols (p. 302).

PCl_5 replaces the two hydroxyl groups by chlorine:—

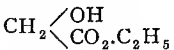


$$CH_2\left\langle\begin{array}{l}OH\\CO.OH\end{array}\right. + 2PCl_5 = CH_2\left\langle\begin{array}{l}Cl\\CO.Cl\end{array}\right. + 2POCl_3 + 2HCl.$$

Glycollic Acid. Glycolyl Chloride, or Chloracetyl Chloride.

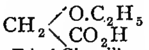
The chlorine in union with CO is very reactive with water and alcohols, yielding free acids and their esters; in the case cited, monochlor-acetic acid, $CH_2Cl.CO_2H$, and its esters result. The remaining chlorine atom is, on the contrary, firmly united, as in ethyl chloride.

The various esters of the dihydric acids exhibit similar relations:—



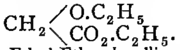
$$CH_2\left\langle\begin{array}{l}OH\\CO_2.C_2H_5\end{array}\right.$$

Ethyl Glycollic Ester.



$$CH_2\left\langle\begin{array}{l}O.C_2H_5\\CO_2H\end{array}\right.$$

Ethyl Glycollic Acid.



$$CH_2\left\langle\begin{array}{l}O.C_2H_5\\CO_2.C_2H_5.\end{array}\right.$$

Ethyl Etho-glycollic Ester.

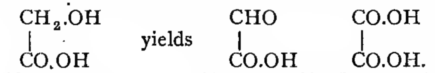
Alkalies cause the alkyl combined with CO_2 to separate, forming ethyl glycollic acid,  $CH_2\left\langle\begin{array}{l}O.C_2H_5\\CO_2H\end{array}\right.$.

See *Berichte*, 15, 162, upon the formation of esters of the oxy-acids.

In the preceding transpositions all the oxy-acids react similarly, but in those following they exhibit variations influenced by the position of the OH group.

Their varying behavior when oxidized is characteristic, especially when chromic acid is employed as the oxidizing agent (p. 203).

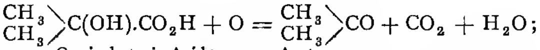
The *primary* oxy-acids, containing the primary alcohol group, $CH_2.OH$, may have the latter converted into aldehyde, and carboxyl groups (p. 117), and the products will then be aldehyde-acids and dicarboxylic acids. Thus, from glycollic acid are derived glyoxylic and oxalic acids:—



$$\begin{array}{c} CH_2.OH \\ | \\ CO.OH \end{array} \quad \text{yields} \quad \begin{array}{c} CHO \\ | \\ CO.OH \end{array} \quad \begin{array}{c} CO.OH \\ | \\ CO.OH. \end{array}$$

Glycollic Acid. Glyoxylic Acid. Oxalic Acid.

The *secondary* oxy-acids, with the secondary alcoholic group, $>CH.OH$, can yield ketones, which, however, pass very readily into other compounds (p. 333). The α-oxy-acids, too, lose carboxyl when boiled with a chromic acid mixture. In them the CO_2H and OH groups are attached to one carbon atom. Should the latter be linked to two hydrocarbon residues, ketones and carbon dioxide are produced:—



$$\left.\begin{array}{l} CH_3 \\ CH_3 \end{array}\right\rangle C(OH).CO_2H + O = \left.\begin{array}{l} CH_3 \\ CH_3 \end{array}\right\rangle CO + CO_2 + H_2O;$$

α-Oxyisobutyric Acid. Acetone.

whereas, if it be in combination with only one such group, aldehydes are first formed:—

$$CH_3.CH(OH).CO_2H + O = CH_3.CHO + CO_2 + H_2O;$$

α-Oxypropionic Acid. Aldehyde.

and these can then be further oxidized to acids.

The α-oxyacids undergo a like decomposition when heated with dilute sulphuric or hydrochloric acid (or by action of concentrated H_2SO_4). Their carboxyl group is removed as formic acid (when concentrated H_2SO_4 is employed, CO and H_2O are the products):—

$$(CH_3)_2C(OH).CO_2H + H_2O = (CH_3)_2CO + HCO_2H,$$
$$CH_3.CH(OH).CO_2H + H_2O = CH_3.CHO + HCO_2H.$$

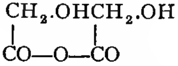
Another alteration is sustained by the α-oxy-acids at the same time; it, however, does not extend far. Water is eliminated and unsaturated acids are produced. This change is easily effected when PCl_3 is allowed to act on the esters of α-oxy-acids (p. 235).

When the β-oxy-acids are heated alone or with acids, water is withdrawn and unsaturated acids are almost the sole products (p. 346):—

$$CH_2(OH).CH_2.CO_2H = CH_2{:}CH.CO_2H + H_2O.$$

β-Oxypropionic Acid. Acrylic Acid.

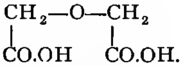
Anhydrides of the Oxy-acids.—The anhydrides of the oxy-acids may be produced in three ways. If two molecules of the acids unite so that the water can be withdrawn from the carboxyl groups, the true or real acid anhydrides are formed. These are perfectly analogous to the anhydrides of the fatty acids (p. 248). If the water should arise from the alcohol hydroxyls, then the products are *alcohol anhydrides* or *anhydridic acids* :—



$$\begin{array}{ccc} CH_2.OH & & CH_2.OH \\ | & & | \\ CO & —O— & CO \end{array}$$

Acid Anhydride,
Glycollic Anhydride.

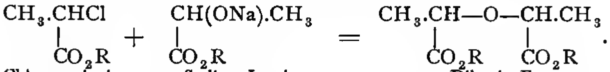
and



$$\begin{array}{ccc} CH_2 & —O— & CH_2 \\ | & & | \\ CO.OH & & CO.OH. \end{array}$$

Alcohol Anhydride,
Diglycollic Acid.

The acid anhydrides of the oxy-fatty-acids have not yet been prepared. The alcohol anhydrides, like diglycollic acid, correspond perfectly to the ethers and sometimes appear on heating the oxy-acids. As a general thing they are prepared according to the same methods as the ethers of the alcohols. Thus diglycollic acid (and some glycollic acid) is obtained from monochloracetic acid, $CH_2Cl.CO_2H$, by the action of bases (lime water or lead oxide); further, dilactic acid (its esters) is made from *a*-chlorpropionic ester and sodium lactic ester :—

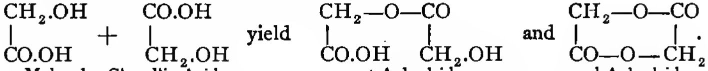


$$\begin{array}{ccccccc} CH_3.CHCl & & CH(ONa).CH_3 & & CH_3.CH & —O— & CH.CH_3 \\ | & + & | & = & | & & | \\ CO_2R & & CO_2R & & CO_2R & & CO_2R \end{array}.$$

a-Chlorpropionic Ester. Sodium Lactic Ester. Dilactic Ester.

These ether acids (anhydridic acids), like the alcohol ethers, break up into oxy-acids on heating them with hydrochloric acid to 100°.

In the *third* class of anhydrides, the *ester anhydrides*, the reaction is between the hydroxyl groups of carboxyl and the alcohol (p. 251). Should *two* molecules of the oxy-acid react we may have the single and double ester formation. Thus, glycollic acid forms a first and second anhydride :—

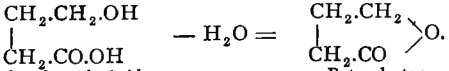


$$\begin{array}{ccccccccccc} CH_2.OH & & CO.OH & & & CH_2 & —O— & CO & & CH_2—O—CO & \\ | & + & | & & \text{yield} & | & & | & \text{and} & |\qquad\quad| & . \\ CO.OH & & CH_2.OH & & & CO.OH & & CH_2.OH & & CO—O—CH_2 & \end{array}$$

2 Molecules Glycollic Acid. 1st Anhydride Glycollic Anhydride. 2d Anhydride Glycolide.

From lactic acid (*a*-oxy-propionic acid), $C_3H_6O_8$, we get lactic anhydride, $C_8H_{10}O_5$, and the so-called *Lactide*, $C_6H_8O_4$ (p. 358). Only the *a*-oxy-acids are capable of entering this simple and double "ester anhydride formation" by the union of two molecules. Heat hastens the reaction (occurs on standing in the dessicator). Conversely the ester anhydrides when heated with water absorb it and the oxy-acids are regenerated.

Should the anhydride formation occur within one and the same molecule of the oxy-acids, we get what are designated *lactones* (*Fittig, Annalen,* **208,** 111; **216,** 27; **226,** 322):—



$$\begin{array}{ccc} CH_2.CH_2.OH & & CH_2.CH_2\diagdown \\ | & -H_2O= & |\qquad\qquad\; >O. \\ CH_2.CO.OH & & CH_2.CO\;\diagup \end{array}$$

γ-Oxy-butyric Acid. γ-Butyrolactone.

The γ- and δ-oxy-acids (from mono- and dicarboxylic acids) especially are adapted to this lactone formation, hence we distinguish

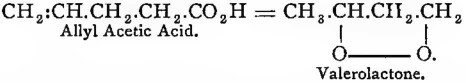
γ- and δ-lactones (*Annalen*, 216, 127). In the first we have a chain of four, in the second a chain of five carbon atoms closed by oxygen. This resembles the union in the anhydrides of the dibasic acids. Generally the lactones are liquids, easily soluble in water, alcohol and ether. They show neutral reaction, possess a faintly aromatic odor, and can be distilled without decomposition. The alkaline carbonates precipitate them from their aqueous solution in the form of oils. The γ-lactones are characterized by great stability. They are partially converted into oxy-acids by water, but this only occurs after protracted boiling, whereas those of the δ-variety gradually absorb water at the ordinary temperature and soon react acid (*Berichte*, 16, 373). Boiling alkaline carbonates convert lactones into oxy-acid salts. The caustic alkalies effect this more readily. If the oxy-acids are freed from their salts by the mineral acids they at once break up into water and lactones. Heat hastens the conversion.

The γ-lactones can be obtained :—

(1) By boiling the γ-halogen fatty acids with water, or with caustic alkalies, and then liberating them with mineral acids. The lactones are produced even in the cold by the action of the alkaline carbonates (p. 346).

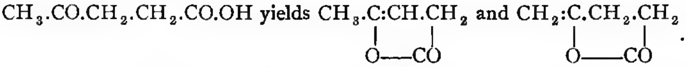
Many γ-derivatives, *e. g.*, γ-chlorbutyric acid (p. 226), decompose directly into lactone and HCl (*Berichte*, 19, Ref. 13) when distilled.

(2) By digesting the unsaturated acids, in which the double union occurs in the $(\beta : \gamma)$ or $(\gamma : \delta)$-position, with hydrobromic or sulphuric acid (diluted with 1 volume H_2O); or by their distillation (*Berichte*, 16, 373; 18, Ref. 229):—



$$\underset{\text{Allyl Acetic Acid.}}{CH_2{:}CH.CH_2.CH_2.CO_2H} = \underset{\text{Valerolactone.}}{\begin{array}{l}CH_3.CH.CH_2.CH_2\\ \quad\;\; | \qquad\quad\;\; |\\ \quad\;\; O\text{———}O.\end{array}}$$

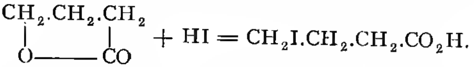
(3) By the action of sodium amalgam upon the γ-ketonic acids, and the decomposition of the sodium salts by mineral acids (see above). Unsaturated lactones are formed upon distilling γ-ketonic acids (*Berichte*, 18, 2263), *e. g.*, the two angelica lactones (p. 343) from lævulinic acid :—



$$CH_3.CO.CH_2.CH_2.CO.OH \text{ yields } \begin{array}{l}CH_3.C{:}CH.CH_2\\ \quad\;\; | \qquad\;\; |\\ \quad\;\; O\text{—}CO\end{array} \text{ and } \begin{array}{l}CH_2{:}C.CH_2.CH_2\\ \quad\;\; | \qquad\;\; |\\ \quad\;\; O\text{—}CO\end{array}.$$

4. Finally, by the distillation of lactone carboxylic acids (splitting-off of CO_2), whereby the isomeric unsaturated acids are also produced, owing to a rearrangement of the atoms.

Some lactones have their lactone union severed, and the elements of a halogen hydride added, through the action of HI, or by heating with hydrochloric or hydrobromic acid. The products in this case are γ-halogen fatty acids (*Berichte* **19**, Ref. 165):—

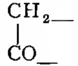


With other lactones this transposition does not occur except in the presence of alcohol. Then the esters of the halogen fatty acids are formed (*Berichte*, **19**, 513). The lactones are reduced to fatty acids upon boiling with hydriodic acid. Ammonia converts them into the amides of the γ-oxyacids, which rapidly regenerate the lactones. Valerolactone, for example, unites with potassium cyanide to form γ-cyanvaleric acid, $CH_3.CH(CN).CH_2.CH_2.CO_2H$ (p. 344 and *Berichte*, **19**, Ref. 439). The lactones do not react with phenylhydrazine.

δ-Caprolactone is the only known member of its class (p. 365).

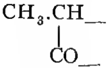
Besides the γ and δ-oxyacids some β-oxyacids (of the benzene series) are capable of yielding corresponding lactones (*Berichte* **16**, 3001; **17**, 415). These β-lactones are much less stable, pass readily into their corresponding oxyacids, and split off carbon dioxide with ease. The existence of an α-lactone seems also to have been demonstrated (*Berichte*, **15**, 579).

The divalent groups, attached to the two hydroxyl groups, in the oxy-acids, are often called radicals:—



$$\begin{array}{l}CH_2—\\ \;|\\ CO—\end{array}$$

Glycolyl.



$$\begin{array}{l}CH_3.CH—\\ \qquad|\\ \quad\; CO—\end{array}$$

Lactyl.

OXY-ACIDS $C_nH_{2n}O_3$.

Carbonic Acid —	CH_2O_3	=	$CO\begin{smallmatrix}\diagup OH\\ \diagdown OH\end{smallmatrix}$
Glycollic Acid or Oxyacetic "	$C_2H_4O_3$	=	$CH_2\begin{smallmatrix}\diagup OH\\ \diagdown CO_2H\end{smallmatrix}$
Lactic Acids or Oxypropionic Acids	$C_3H_6O_3$	=	$C_2H_4\begin{smallmatrix}\diagup OH\\ \diagdown CO_2H\end{smallmatrix}$
Oxybutyric Acids	$C_4H_8O_3$	=	$C_3H_6\begin{smallmatrix}\diagup OH\\ \diagdown CO_2H\end{smallmatrix}$
Oxyvaleric "	$C_5H_{10}O_3$	=	$C_4H_8\begin{smallmatrix}\diagup OH\\ \diagdown CO_2H,\end{smallmatrix}$

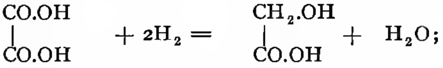
etc., etc.

1. **Carbonic Acid,** CH_2O_3—oxyformic acid—is the lowest member of the series. It cannot exist free, and its character varies considerably from those of the rest. From its symmetrical structure, $CO\begin{smallmatrix}\diagup OH\\ \diagdown OH\end{smallmatrix}$, and the fact that no difference exists in the OH groups, this compound is a *dibasic* acid, although very feeble.

Therefore it and its numerous derivatives will be treated later, after the other dihydric acids.

2. **Glycollic Acid**, $C_2H_4O_3 = CH_2(OH).CO_2H$.

Glycollic, or oxyacetic acid, is obtained according to the methods given as follows: from ethylene glycol, from monochlor- or brom-acetic acid, and from amido-acetic acid, $CH_2(NH_2).CO_2H$, by means of nitrous acid. It is produced, also, when nascent hydrogen (zinc and sulphuric acid) acts upon oxalic acid:—



$$\begin{array}{l}CO.OH\\ |\\ CO.OH\end{array} + 2H_2 = \begin{array}{l}CH_2.OH\\ |\\ CO.OH\end{array} + H_2O;$$

by oxidizing ethyl alcohol with nitric acid at ordinary temperatures (with glyoxal and glyoxylic acid, p. 330); from glycosin and its derivatives, and from glycerol by the action of silver oxide (*Berichte*, **16**, 2414).

The best method of preparing the acid is to boil chloracetic acid with alkalies or calcium carbonate. The calcium salt first formed is decomposed with an equivalent amount of oxalic acid and the filtrate concentrated (*Berichte*, **16**, 2954).

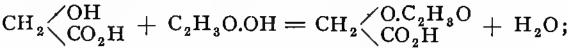
Glycollic acid is a thick syrup, which gradually crystallizes upon standing over sulphuric acid. The crystals melt at 80° and deliquesce in the air. It dissolves easily in water, alcohol and ether. When distilled it decomposes with formation of paraformaldehyde (p. 192).

Its alkali salts are very deliquescent. The *calcium salt*, $(C_2H_3O_3)_2Ca$, with 3 and 4 H_2O, is sparingly soluble in cold water (1 part in 8 parts H_2O at 10°), and crystallizes in needles. The *silver salt*, $(C_2H_3O_3Ag)_2 + H_2O$, is also rather insoluble. The *ethyl ester*, $CH_2(OH).CO_2.C_2H_5$, is a liquid, possessiog a specific gravity equal to 1.03, and boils at 150°.

Alcohol and acid radicals can replace the hydrogen in alcohol-hydroxyl of glycollic acid.

The *acid derivatives* are formed:—

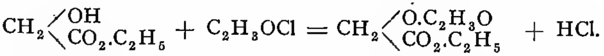
(1) On heating glycollic acid with monobasic acids:—



$$CH_2\begin{cases}OH\\ CO_2H\end{cases} + C_2H_3O.OH = CH_2\begin{cases}O.C_2H_3O\\ CO_2H\end{cases} + H_2O;$$

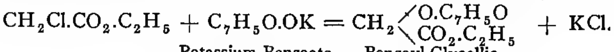
Acetoglycollic Acid.

or by acting upon esters of the acid with acid chlorides:—



$$CH_2\begin{cases}OH\\ CO_2.C_2H_5\end{cases} + C_2H_3OCl = CH_2\begin{cases}O.C_2H_3O\\ CO_2.C_2H_5\end{cases} + HCl.$$

(2) By action of the alkali salts of acids upon esters of monochlor-acetic acid:—



$$CH_2Cl.CO_2.C_2H_5 + C_7H_5O.OK = CH_2\begin{cases}O.C_7H_5O\\ CO_2.C_2H_5\end{cases} + KCl.$$

Potassium Benzoate. Benzoyl Glycollic Ester.

We obtain the *alcohol derivatives* when sodium alcoholates act on monochloracetic acid:—

$$CH_2Cl.CO_2Na + C_2H_5.ONa = CH_2\Big\langle{O.C_2H_5 \atop CO_2Na} + NaCl.$$

Ethyl Glycollic Acid.

Methyl Glycollic Acid, $CH_2\Big\langle{O.CH_3 \atop CO_2H}$, boils at 198°; ethyl glycollic acid, $CH_2(O.C_2H_5).CO_2H$, at 206°. Both are very stable, and boiling alkalies do not decompose them.

The *ether-esters*, like $CH_2\Big\langle{O.CH_3 \atop CO_2.CH_3}$, result when chloracetic esters are acted upon by sodium alcoholates. For their boiling points see *Berichte*, 17, 486.

Thioglycollic Acid, $CH_2\Big\langle{SH \atop CO_2H}$, is both an acid and a mercaptan. It is obtained from monochloracetic acid and potassium sulphydrate; from thiohydantoïn (see this), and its phenyl derivatives, when they are heated with alkalies (*Annalen*, 207, 124). It is an oil, which is readily soluble in water, alcohol and ether. Heat decomposes it. On adding ferric chloride to the acid solution, then neutralizing with ammonia, we obtain a purple-red coloration. Thioglycollic acid behaves like a dibasic acid, forming primary and secondary salts. This is due to the SH group imparting the properties of the mercaptans. The *barium salt*, $CH_2\Big\langle{S \atop CO_2}\Big\rangle Ba + 3H_2O$, dissolves with difficulty in water.

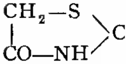
The acid (its alkali salts), on exposure to the air, oxidizes to—

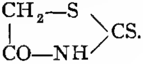
Dithiodiglycollic Acid, $S_2\Big\langle{CH_2.CO_2H \atop CH_2.CO_2H}$. It may also be produced by oxidation with ferric chloride, or by the action of iodine upon potassium thioglycollate (*Berichte*, 19, 114). It is crystalline and fuses at 100° C.

Thiodiglycollic Acid, $S\Big\langle{CH_2.CO_2H \atop CH_2.CO_2H}$, results from the action of chloracetic acid upon potassium sulphide. It crystallizes in plates and melts at 129°. Potassium permanganate oxidizes it to sulphodiacetic acid, $SO_2\Big\langle{CH_2.CO_2H \atop CH_2.CO_2H}$. The latter exhibits a deportment analogous to that observed with aceto-acetic acid, in that its CH_2-group is very reactive (*Berichte*, 18, 3241 and p. 307).

Thioglycollic acid, and also thioacetic acid (p. 262), like the mercaptans (p. 306), unite with the aldehydes, ketones and ketonic acids to form compounds of the type, $R_2.C\Big\langle{S.CH_2.CO_2H \atop S.CH_2.CO_2H}$. Boiling concentrated hydrochloric acid resolves them into their components (*Berichte*, 21, 478).

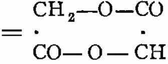
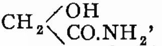
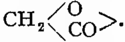
Thiocyanacetic Acid, $CH_2\Big\langle{S.CN \atop CO_2H}$, **Sulphocyanacetic Acid,** is formed by the action of chloracetic acid upon KCNS. It is a thick oil. Its *ethyl ester*, from chloracetic ester, boils about 220° C.

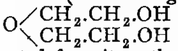
On boiling the latter (or thiohydantoïn) with concentrated hydrochloric acid, rhodanacetic acid, $CH_2\Big\langle{N:CS \atop CO_2H}$, is formed. This acid should probably be viewed as *pseudo-dioxythiazole*,  (*Berichte*, 22, Ref. 19). Large leaflets, melting at 128°. It forms a benzylidene compound with benzaldehyde (*Berichte*, 22, Ref. 333).

Rhodanic Acid,  $CH_2<\begin{matrix}SH\\CO.S.CN\end{matrix}$, the mixed anhydride of thioglycollic (see above) and sulphocyanic acids, is obtained by the action of $CNS(NH_4)$ upon chloracetic acid. It consists of yellow prisms or plates, and melts at 169° with decomposition. Upon digestion with baryta water it splits up into thioglycollic and hydro-sulphocyanic acids (*Berichte*, 19, 114; 22, Ref. 334). It, in all probability, represents a *thioxythiazole*, 

Anhydrides of Glycollic Acid.

Glycollic Anhydride, $C_4H_6O_5 = CH_2(OH).CO.O.CH_2.CO_2H$, the first ester anhydride of glycollic acid (p. 354), is produced on heating glycollic acid to 100°. It is a solid, insoluble in alcohol, water and ether. It melts at 128–130°. Boiling water changes it to glycollic acid.

Glycolide, $C_4H_4O_4 =$  —the second ester anhydride of glycollic acid (p. 354)—is obtained by strongly igniting glycollic acid (to 250°) or tartronic acid, and by heating potassium or silver glycollate (*Berichte*, 14, 577). It forms a powder almost insoluble in water, and melts at 220°. It returns to glycollic acid when boiled with water. When heated with ammonia it yields glycolamide,  $CH_2<\begin{matrix}OH\\CO.NH_2\end{matrix}$, which boils at 120°. Formerly glycolide was supposed to be an ester anhydride (p. 351) with the formula,  $CH_2<\begin{matrix}O\\CO\end{matrix}>$. The present double formula is assigned it from its analogy to lactide (p. 359).

Diglycollic Acid, $C_4H_6O_5$, the alcohol anhydride of glycollic acid (p. 351), is formed on boiling monochloracetic acid with lime, baryta, magnesia, or lead oxide (also with glycollic acid), and in the oxidation of diethylene glycol,  $O<\begin{matrix}CH_2.CH_2.OH\\CH_2.CH_2.OH\end{matrix}$ (p. 304), with nitric acid and platinum sponge. When separated from its rather insoluble calcium salt with sulphuric acid, diglycollic acid crystallizes in rhombic prisms, which melt at 148°. Boiling alkalies do not alter it. It is only when heated with concentrated hydrochloric acid to 120° that it breaks up into glycollic acid. The acid is dibasic, yielding primary and secondary salts.

3. Lactic Acids, or Oxypropionic Acids, $C_3H_6O_3$.

There are two possible isomerides:—

$CH_3.CH(OH).CO_2H$	and	$CH_2(OH).CH_2.CO_2H$
α-Oxypropionic Acid. Ethidene Lactic Acid.		β-Oxypropionic Acid. Ethylene Lactic Acid.

(1) **Ethidene Lactic Acid, Ordinary Lactic Acid of Fermentation,** $CH_3.CH(OH).CO_2H$, is formed by a peculiar fermentation of sugar (milk sugar, cane sugar), gum and starch, in the

presence of albuminoid substances (chiefly caseïn). It is, therefore, contained in many substances which have soured, *e, g.*, in sour milk, in sour-kraut, pickles, also in the gastric juice. The lactic fermentation occurs by the action of a particular, organized ferment, at temperatures from 35–45°. Excess of free acid arrests it, but it is renewed, if the acid be neutralized by alkalies.

The acid is artificially prepared by the methods already described, p. 347:—from α-chlor- or brom-propionic acid by boiling with alkalies; from α-propylene glycol by oxidation with nitric acid; from alanine, $CH_3.CH(NH_2).CO_2H$, by means of nitrous acid, and by the action of nascent hydrogen upon racemic acid. Other methods consist in heating grape sugar and cane sugar with water and 2–3 parts barium hydrate, to 160°, and α-dichloracetone, $CH_3.CO.CHCl_2$, with water to 200°.

Preparation.—Lactic acid is usually obtained by the fermentation of cane sugar. 2 Kilograms of cane sugar and 15 grams of tartaric acid are dissolved in 17 litres of water, and the solution allowed to stand several days. Then add 100 grams decaying cheese, previously macerated in 4 litres of sour milk, and 1200 grams zinc-white, and let the mixture ferment at 40°–45° for 8–10 days (longer fermentation changes the lactic into butyric acid). The entire mass is next brought to boiling, filtered, and the filtrate strongly concentrated. The zinc lactate which separates out is decomposed by H_2S, the zinc sulphide removed by filtration, and the filtrate containing the lactic acid evaporated on the water bath. To separate the lactic acid produced in this manner from the mannitol (formed simultaneously) dissolved by it, shake the residue with ether, which will not dissolve the mannitol.

Fermentation lactic acid is a thick syrup, with a specific gravity 1.215, but it cannot be obtained crystallized. It is miscible with water, alcohol and ether, and absorbs moisture when exposed to the air. Placed in a dessicator over sulphuric acid it partially decomposes into water and its anhydride. When distilled it yields lactide, aldehyde, carbon monoxide and water.

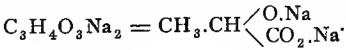
It is optically inactive. Penicillium glaucum converts its ammonium salt into active sarcolactic acid (Lewkowitsch, *Berichte*, 16, 2720).

Heated to 130° with dilute sulphuric acid it decomposes into aldehyde and formic acid (p. 350); when oxidized with chromic acid, acetic acid and carbon dioxide are formed. Heated with hydrochloric acid, it changes to α-brompropionic acid:

$$CH_3.CH(OH).CO_2H + HBr = CH_3.CHBr.CO_2H + H_2O.$$

Hydriodic acid at once reduces it to propionic acid.

The *sodium salt*, $C_3H_5O_3Na$, is an amorphous mass. When heated with metallic sodium, the alcoholic hydrogen is replaced, and we get the *disodium compound*:



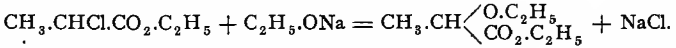
$$C_3H_4O_3Na_2 = CH_3.CH\left\langle\begin{matrix}O.Na\\CO_2.Na\end{matrix}\right.$$

The *calcium salt*, $(C_3H_5O_3)_2Ca + 5H_2O$, crystallizes in hard warts, consisting of concentrically grouped needles. It is soluble in ten parts cold water, and is very readily dissolved by hot water and alcohol.

The *zinc salt*, $(C_3H_5O_3)_2Zn + 3H_2O$, crystallizes in shining needles, which dissolve in 58 parts cold and 6 parts hot water. The *iron salt*, $(C_3H_5O_3)_2Fe + 3H_2O$, is very sparingly soluble in water, and yields crusts consisting of delicate needles. It is also obtained by boiling whey with iron filings. The salts of *lactic acid* are called *lactates*.

Ethyl Lactic Ester, $CH_3.CH(OH).CO_2.C_2H_5$, is formed when lactic acid and anhydrous alcohol are heated to 170°. It is a neutral liquid, which boils at 156°. It is soluble in water, and rapidly decomposes into lactic acid and alcohol. When potassium and sodium act upon the ester, they replace alcoholic hydrogen, and if the product be treated with ethyl iodide we obtain:—

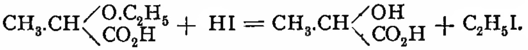
Ethyl Etholactic Ester, $CH_3.CH{<}\begin{matrix}O.C_2H_5\\CO_2.C_2H_5\end{matrix}$. This is formed also on heating α-chlorpropionic ester (or lactyl chloride) with sodium ethylate:—



$$CH_3.CHCl.CO_2.C_2H_5 + C_2H_5.ONa = CH_3.CH{<}\begin{matrix}O.C_2H_5\\CO_2.C_2H_5\end{matrix} + NaCl.$$

It boils at 156°, and is insoluble in water. When the ester is boiled with caustic soda ethyl-lactic acid is produced.

Ethyl Lactic Acid, $CH_3.CH{<}\begin{matrix}O.C_2H_5\\CO_2H\end{matrix}$. A strongly acid syrup, yielding crystalline salts, which revert to the diethyl ester when acted upon with ethyl iodide. Hydriodic acid breaks it up into lactic acid and ethyl iodide:—



$$CH_3.CH{<}\begin{matrix}O.C_2H_5\\CO_2H\end{matrix} + HI = CH_3.CH{<}\begin{matrix}OH\\CO_2H\end{matrix} + C_2H_5I.$$

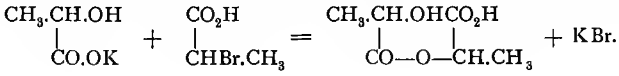
Aceto-lactic Acid, $CH_3.CH{<}\begin{matrix}O.C_2H_3O\\CO_2H\end{matrix}$, occurs together with sarcolactic acid in beef extract. It results from the interaction of lactic acid, as well as of sarcolactic acid, with acetic acid. Its amorphous zinc salt distinguishes it from the other lactic acids (*Berichte*, 22, 2711).

On adding lactic acid to a mixture of nitric and sulphuric acids (p. 349) it dissolves, forming *nitrolactic acid*, $CH_3.CH{<}\begin{matrix}O.NO_2\\CO_2H\end{matrix}$. A yellow liquid, slightly soluble in water. It decomposes readily. Its specific gravity equals 1.35.

Lactyl Chloride, $CH_3.CH{<}\begin{matrix}Cl\\CO.Cl\end{matrix}$, α-chlorpropionyl chloride, is obtained by the distillation of dry lime lactate (1 part) with PCl_5 (2 parts). It is imperfectly separated from the PCl_3O which is formed at the same time. With water it yields α-chlorpropionic acid; with alcohol α-chlorpropionic ester. Lactic acid is regenerated when the chloride is heated with alkalies.

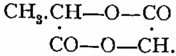
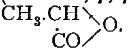
ANHYDRIDES OF LACTIC ACID.

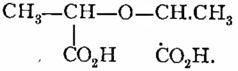
Lactic Anhydride, $C_6H_{10}O_5$, is the first ester anhydride of lactic acid (p. 351). It is formed when lactic acid is heated to 130°, or when it stands over sulphuric acid; further, by the action of potassium lactate upon α-brompropionic acid:—



$$\begin{array}{l}CH_3.CH.OH\\ \quad|\\ \quad CO.OK\end{array} + \begin{array}{l}CO_2H\\ |\\ CHBr.CH_3\end{array} = \begin{array}{l}CH_3.CH.OHCO_2H\\ \quad|\qquad\quad|\\ \quad CO{-}O{-}CH.CH_3\end{array} + KBr.$$

It is an amorphous powder, almost insoluble in water. The alkalies immediately convert it into lactic acid.

Lactide, $C_6H_8O_4$ =  $\begin{array}{l} CH_3.CH{-}O{-}CO \\ \quad\;\;\; \vdots \qquad\quad\; \vdots \\ \quad\;\;\; CO{-}O{-}CH.CH_3 \end{array}$, the second ester anhydride, is obtained by distilling lactic acid, or by passing dry air through the acid heated to 150°. It crystallizes from alcohol in rhombic plates, melting at 124.5° and boiling at 255°. It dissolves slowly in water with gradual formation of lactic acid. The vapor density agrees with the formula, $C_6H_8O_4$ (*Berichte*, 7, 755). It was formerly believed that it was "an inner anhydride,"  $\begin{array}{l} CH_3.CH\diagdown \\ \qquad\;\;\; \vdots \quad\; {>}O. \\ \qquad\;\; CO\diagup \end{array}$

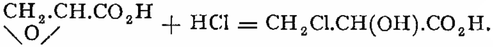
Dilactic Acid, $C_6H_{10}O_5$ =  $\begin{array}{l} CH_3{-}CH{-}O{-}CH.CH_3 \\ \qquad\quad | \qquad\quad\;\; \vdots \\ \qquad CO_2H \quad\; CO_2H. \end{array}$ The diethyl ester is produced on heating α-brompropionic ester with sodium lactic ester (p. 351), in alcoholic solution. It boils at 235°, and when heated above 100° with water, breaks up into lactic acid and alcohol.

Substituted Lactic Acids :—

β-Chlorlactic Acid, $CH_2Cl.CH(OH).CO_2H = C_3H_5ClO_3$, is formed by the oxidation of epichlorhydrin and α-chlorhydrin, $CH_2Cl.CH(OH).CH_2.OH$, with concentrated HNO_3; by the addition of hypochlorous acid to acrylic acid (together with α-chlorhydracrylic acid (p. 362) :—

$$\underset{\text{Acrylic Acid.}}{CH_2{:}CH.CO_2H} \text{ yields } \underset{\beta\text{-Chlorlactic Acid.}}{CH_2Cl.CH(OH).CO_2H} \text{ and } \underset{\alpha\text{-Chlorhydracrylic Acid.}}{CH_2(OH).CHCl.CO_2H};$$

and by the addition of HCl to epihydrinic acid (glycidic acid) :—

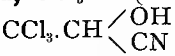


$$\begin{array}{l} CH_2.CH.CO_2H \\ \;\diagdown O \diagup \end{array} + HCl = CH_2Cl.CH(OH).CO_2H.$$

Brom- and iod- acetic acids are obtained in the same manner (*Berichte*, 14, 937). The first melts at 89°–90°, the second at 100°–101°. β-Chlorlactic acid is also formed from monochloraldehyde by the action of hydrocyanic and hydrochloric acids (p. 347).

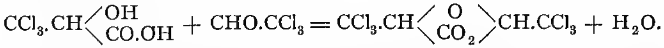
β-Chlorlactic acid crystallizes from water in large transparent plates or prisms, and melts at 78°–79°. Silver oxide converts it into glyceric acid; when reduced with hydriodic acid it becomes β-iodpropionic acid. Heated with alcoholic potash it is again changed to epihydrinic acid (see above), just as ethylene oxide is obtained from glycolchlorhydrin (p. 300).

Dichlorlactic Acid, $CHCl_2.CH(OH).CO_2H$, is obtained from dichloraldehyde through the cyanide (p. 347). It forms deliquescent plates, melting at 77°. It reduces ammoniacal silver solutions.

Trichlorlactic Acid, $CCl_3.CH(OH).CO_2H$, is made by heating chloralcyanhydrin,  $CCl_3.CH\begin{array}{l}\diagup OH \\ \diagdown CN\end{array}$ (p. 196), with concentrated hydrochloric acid (*Berichte*, 17, 1997). It is a crystalline mass, melting at 105°–110°, and soluble in water, alcohol and ether. Alkalies easily change it to chloral, chloroform and formic acid. Zinc and hydrochloric acid reduce it to dichlor- and mono-chloracrylic acids (p. 237). Its ethyl ester melts at 66°–67°, and boils at 235°. The best method of preparing it consists in heating chloralcyanhydrin with alcohol and sulphuric acid (or HCl, *Berichte*, 18, 754).

Because trichlorlactic acid yields chloral without difficulty, it is converted quite readily, by different reactions, into derivatives of chloral and glyoxal. It forms glyoximes with hydroxylamine, and glycosin with ammonia (p. 325, and *Berichte*, 18, 754).

When trichlorlactic acid is heated to 150° with excess of chloral, we obtain *trichlorethidene-trichlorlactic ester* :—

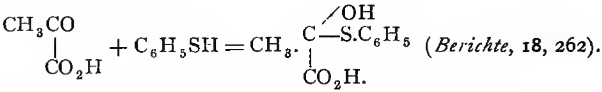


$$CCl_3.CH\left\langle\begin{matrix}OH\\CO.OH\end{matrix}\right. + CHO.CCl_3 = CCl_3.CH\left\langle\begin{matrix}O\\CO_2\end{matrix}\right\rangle CH.CCl_3 + H_2O.$$

The same body, $C_5H_2Cl_6O_3$, called **Chloralide**, was at first prepared by heating chloral (1 part) with fuming sulphuric acid (3 parts) to 105°. It crystallizes from alcohol and ether in large prisms, is insoluble in water, melts at 114°–115° and boils at 272°–273°. When heated to 140° with alcohol, it breaks up into trichlorlactic ester and chloral alcoholate. Chloral also unites with lactic and other oxy-acids, like glycollic, malic, salicylic, etc., forming the so-called *chloralides* (*Annalen*, 193, 1).

Tribromlactic Acid, $CBr_3.CH(OH).CO_2H$, from bromal cyanhydrin, melts at 141°-143° and unites with chloral and bromal to corresponding chloralides and bromalides.

a **Thio-lactic Acid**, $CH_3.CH(SH).CO_2H$, **Thio-dilactic Acid**, $S\left\langle\begin{matrix}CH(CH_3).CO_2H\\CH(CH_3).CO_2H\end{matrix}\right.$ and **Dithiodilactic Acid**, $S_2\left\langle\begin{matrix}CH(CH_3).CO_2H\\CH(CH_3).CO_2H\end{matrix}\right.$, are obtained from *α*-chlorpropionic acid by methods analogous to those employed with thioglycollic acids (p. 318). They can also be prepared from racemic acid by the action of hydrogen sulphide. Racemic acid yields *alkyl-thio-oxypropionic acids*, with the mercaptans:—



$$\begin{matrix}CH_3CO\\|\\CO_2H\end{matrix} + C_6H_5SH = CH_3.\begin{matrix}\diagup OH\\C-S.C_6H_5\\|\\CO_2H.\end{matrix}$$

(*Berichte*, 18, 262).

Cysteïn is probably an *amido-thiolactic acid*, $CH_3.C\left(\begin{matrix}SH\\NH_2\end{matrix}\right).CO_2H$. It is obtained from cystin by reduction with tin and hydrochloric acid. A crystalline powder, very soluble in water, and yielding an indigo-blue color with ferric chloride. In the air it rapidly oxidizes to cystin (*Berichte*, 18, 258, and 19, 125).

Cystin, $C_6H_{12}N_2O_4S_2$, probably dithio-diamido-dilactic acid, $S_2\left\langle\begin{matrix}C(CH_3)(NH)_2.CO_2H\\C(CH_3)(NH)_2.CO_2H\end{matrix}\right.$, occurs in some calculi and urinary sediments. It forms colorless leaflets. It is insoluble in water and alcohol, but dissolves in acids and alkalies.

The **Mercapturic Acids** (*Berichte*, 18, 258) are probably acetyl compounds of alkyl-thio-lactic acids.

Sarco-lactic or **Paralactic Acid** is a peculiar modification of fermentation lactic acid. It is present in different animal organs, especially in the juice of the flesh. Liebig's Beef Extract furnishes it. In all its transpositions it behaves like ordinary lactic acid, hence we must accept the same chemical structure for it. The existence of the two modifications is explained by the asymmetry of a carbon atom in the acid (p. 63). Sarco-lactic acid is distinguished from the ordinary variety by turning the plane of polarization to the right (the ordinary acid is inactive) and by differences in its salts. When heated to 130° it yields lactic anhydride (p. 358), which water changes back to ordinary lactic acid.

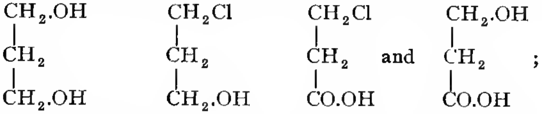
Its *calcium salt*, $(C_3H_5O_3)_2Ca$, contains four molecules of water, and is more sparingly soluble in water than that of ordinary lactic acid. The *zinc salt* contains two molecules of water, yields shining, thick prisms and is more soluble (1 part in 17 parts H_2O at 15°) in water than the zinc salt of ordinary lactic acid.

---

2. **Ethylene Lactic Acid,** or **Hydracrylic Acid,** $CH_2(OH).CH_2.CO_2H$, β-oxypropionic acid, is obtained from β-iodpropionic acid on heating it with moist silver oxide, or on boiling with water:—

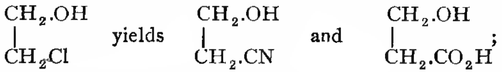
$$\underset{\beta\text{-Iodpropionic Acid.}}{CH_2I.CH_2.CO_2H} + AgOH = \underset{\beta\text{-Oxypropionic Acid.}}{CH_2(OH).CH_2.CO_2H} + AgI;$$

by the careful oxidation of β-propylene glycol (p. 308), or by conversion of the same into chlorhydrin and β-chlorpropionic acid:—



$$\begin{array}{c} CH_2.OH \\ | \\ CH_2 \\ | \\ CH_2.OH \end{array} \qquad \begin{array}{c} CH_2Cl \\ | \\ CH_2 \\ | \\ CH_2.OH \end{array} \qquad \begin{array}{c} CH_2Cl \\ | \\ CH_2 \\ | \\ CO.OH \end{array} \quad \text{and} \quad \begin{array}{c} CH_2.OH \\ | \\ CH_2 \\ | \\ CO.OH \end{array} \; ;$$

by the action of CNK and HCl upon ethylene chlorhydrin:—



$$\begin{array}{c} CH_2.OH \\ | \\ CH_2Cl \end{array} \quad \text{yields} \quad \begin{array}{c} CH_2.OH \\ | \\ CH_2.CN \end{array} \quad \text{and} \quad \begin{array}{c} CH_2.OH \\ | \\ CH_2.CO_2H \end{array} \; ;$$

and from ethylene oxide through the agency of CNH and HCl. The formation of the acid from acrylic acid by heating with aqueous sodium hydroxide to 100° is also very interesting.

The free acid yields a non-crystallizable, thick syrup. When heated alone, or when boiled with sulphuric acid (diluted with 1 part H_2O), it loses water and forms acrylic acid (hence the name hydracrylic acid, p. 350):—

$$CH_2(OH).CH_2.CO_2.H = CH_2{:}CH.CO_2H + H_2O.$$

Hydriodic acid again changes it to β-iodpropionic acid. It yields oxalic acid and carbon dioxide when oxidized with chromic acid or nitric acid.

The *sodium salt*, $C_3H_5O_3Na$, is indistinctly crystalline, and melts without change at 142–143°. It loses water at 150°, and forms sodium acrylate. The *calcium salt*, $(C_3H_5O_3)_2Ca + 2H_2O$, forms large rhombic prisms, loses its water of crystallization at 100°, and fuses at 140–145° without decomposition. Heated to 190° it parts with water and becomes calcium acrylate. The *zinc salt*, $(C_3H_5O_3)_2Zn + 4H_2O$, crystallizes from a moderately concentrated solution, in large, shining prisms, and dissolves in an equal part of water at 15°. If the solution is very concentrated it will only crystallize with difficulty. The zinc salt is soluble in alcohol, whereas the latter precipitates zinc α-lactate and paralactate.

α-Chlorhydracrylic Acid, $CH_2(OH).CHCl.CO_2H$, from acrylic acid, is a liquid, and is converted into hydracrylic acid by nascent hydrogen; it yields glycidic acid with the alkalies.

4. Oxybutyric Acids, $C_4H_8O_3 = C_3H_6(OH).CO_2H$.

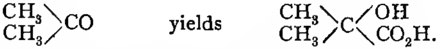
Four of the five possible oxybutyric acids are known:—

(1) **α-Oxybutyric Acid**, $CH_3.CH_2.CH(OH).CO_2H$, is obtained by boiling α-brombutyric acid with moist silver oxide or caustic potash, and from propionic aldehyde with hydrocyanic and hydrochloric acids. It is crystalline and deliquescent in the air. It melts at 43–44°. The *zinc salt*, $(C_4H_7O_3)_2Zn + 2H_2O$, crystallizes from water in white leaflets, sparingly soluble in cold water. When oxidized with chromic acid, the acid decomposes into propionic acid and CO_2.

(2) **β-Oxybutyric Acid**, $CH_3.CH(OH).CH_2.CO_2H$, is formed by the action of sodium amalgam upon aceto-acetic ester (p. 338), by the oxidation of aldol (p. 321) with silver oxide, and from α-propylene chlorhydrin, $CH_3.CH(OH).CH_2Cl$, (p. 308) by the action of CNK and subsequent saponification of the cyanide. It is a thick, non-crystallizable syrup, which volatilizes with steam. The Ca- and Zn-*salts* are amorphous and readily soluble in water. When heated the acid decomposes (like all β-oxy-acids, p. 350) into water and crotonic acid, $CH_3.CH:CH.CO_2H$. An optically active β-oxybutyric acid has been isolated from diabetic urine (*Berichte*, 18, Ref. 451).

(3) **γ-Oxybutyric Acid**, $CH_2(OH).CH_2.CH_2.CO_2H$, is not very stable in a free condition, because it readily breaks up, like all γ-oxy-acids (p. 351) into water and its inner anhydride **butyrolactone**, $C_4H_6O_2$. The acid (its salts) is obtained by letting sodium amalgam act on succinyl chloride, $C_2H_4(CO.Cl)_2$, and from the bromhydrin of β-propylene glycol (p. 308) by means of CNK and the after-saponification of the cyanide, and from butyrolactone carboxylic acid (see this), by the splitting-off of CO_2 (*Berichte*, 16, 2592); by the distillation of γ-chlorbutyric acid (p. 352); and from the reaction product of ethylene chlorhydrin and aceto-acetic ester by decomposing it with baryta (*Berichte*, 18, Ref. 26). Butyrolactone, obtained from its salts, is a neutral, thick liquid, boiling at 203°; its specific gravity equals 1.130 at 20°. It is miscible with water, and is precipitated by soda.

(4) α-**Oxyisobutyric Acid**, $\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right>C(OH).CO_2H$, was first obtained by the action of CNH and HCl on acetone (p. 203), hence called *acetonic acid:*—



$$\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right>CO \quad \text{yields} \quad \left.\begin{matrix}CH_3\\CH_3\end{matrix}\right>C\left<\begin{matrix}OH\\CO_2H.\end{matrix}\right.$$

It is further obtained from acetone chloroform (p. 205); from oxalic ester by the action of CH_3I and Zn (see p. 347), hence termed dimethyloxalic acid, or better, dimethyl-oxyacetic acid; from α-bromisobutyric acid on boiling with baryta water:—

$$(CH_3)_2CBr.CO_2H + H_2O = (CH_3)_2C(OH).CO_2H + HBr:$$

from β-isoamylene glycol by oxidation with nitric acid (p. 310) (hence called butyl lactic acid), and from isobutyric acid, $C_4H_8O_2$, by oxidizing with potassium permanganate (p. 227). Oxy-isobutyric acid crystallizes in prisms and is very soluble in water and ether. It sublimes at 50°, in long needles, melts at 79° and distils at 212°. Methacrylic acid is formed when PCl_3 acts on its esters (p. 240). When oxidized with chromic acid, it breaks up into acetone and carbon dioxide.

The *barium salt*, $(C_4H_7O_3)_2Ba$, consists of easily soluble shining needles. The *zinc salt*, $(C_4H_7O_3)_2Zn + 2H_2O$, crystallizes in microscopic, six-sided plates, sparingly soluble in water.

(5) β-**Oxyisobutyric Acid**, $CH_2.OH.CH(CH_3).CO_2H$, has not been obtained.

5. Oxyvaleric Acids, $C_5H_{10}O_3 = C_4H_8(OH).CO_2H$.

(1) α-**Oxyvaleric Acid**, $CH_3.CH_2.CH_2.CH(OH).CO_2H$, has been obtained from normal α-bromvaleric acid and from normal butyric aldehyde. It forms table-like crystals, melting at 28–29° (*Berichte*, 18, Ref. 79).

(2) γ-**Oxyvaleric Acid**, $CH_3.CH(OH).CH_2.CH_2.CO_2H$, like all the γ-oxyacids, decomposes when separated from its salts into water and its inner anhydride, *valerolactone*, $C_5H_8O_2$ (p. 352). The latter is prepared directly from γ-bromvaleric acid (from allyl acetic acid, p. 241), on heating it with water above 100°. It may be obtained more readily by acting on β-aceto-propionic acid (lævulinic acid, p. 343), with sodium amalgam and water. Sulphuric acid is added to the solution and the latter shaken with ether. Valerolactone is a colorless liquid which does not solidify at —18°, and boils at 206–207°. It is miscible with water, forming a neutral solution from which it is reprecipitated by alkaline carbonates. When boiled with alkalies, baryta or lime it forms γ-oxyvalerates. It yields succinic acid when oxidized with nitric acid (*Annalen*, 208, 104).

(3) α-**Oxyisovaleric Acid**, $(CH_3)_2.CH.CH(OH).CO_2H$, is obtained from α-bromisovaleric acid and from isobutyraldehyde, $(CH_3)_2CH.CHO$, by means of CNH and HCl. It crystallizes in large rhombic plates, which melt at 86° and volatilize

at 100°. Its *ethyl ester*, boiling at 175°, is obtained from oxalic ester by zinc and isopropyl iodide. Heated with sulphuric acid it decomposes into isobutyraldehyde and formic acid, and when oxidized with chromic acid it yields isobutyric acid and CO_2. Heated to 200° it affords an anhydride, $(C_5H_8O_2)_2$ (?) (p. 358), resembling lactide. It melts at 136°.

(4) β-**Oxyisovaleric Acid**, $(CH_3)_2C(OH).CH_2.CO_2H$, is formed on oxidizing dimethyl allylcarbinol (p. 121) with chromic acid, or isopropyl acetic acid, $(CH_3)_2.CH.CH_2.CO_2H$, with an alkaline $KMnO_4$ solution (p. 346). It is a liquid which is not volatile with steam. Chromic acid oxidizes it to acetone, acetic acid and carbon dioxide.

(5) **Methyl-ethyl Oxyacetic Acid**, $\begin{matrix}CH_3\\C_2H_5\end{matrix}\!\!>\!C(OH).CO_2H$, α-methyl-α-oxybutyric acid, is obtained from methyl-ethyl acetic acid (p. 229), by oxidation with a solution of potassium permanganate; from oxalic ester by means of CH_3I, C_2H_5I and zinc; and from methyl-ethyl ketone by means of CNH and HCl. It is crystalline, melts at 68°, and sublimes at 100°. Hydriodic acid reduces it to methyl-ethyl acetic acid, while CrO_3 oxidizes it to methyl-ethyl ketone and CO_2. Its *ethyl ester* boils at 165°.

(6) α-**Methyl**-β-**oxybutyric Acid**, $\begin{matrix}CH^3\\CH_3.CH(OH)\end{matrix}\!\!>\!CH.CO_2H$, is obtained from methyl aceto acetic ester, $CH_3.CO.CH(CH_3).CO_2.C_2H_5$ (p. 340). It is a liquid, which decomposes, when distilled or if heated with HI, into water and methyl crotonic acid.

6. **Oxycaproic Acids**, $C_6H_{12}O_3 = C_5H_{10}(OH).CO_2H$.

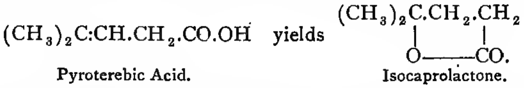
(1) α-**Oxycaproic Acid**, $CH_3.(CH_2)_3.CH(OH).CO_2H$, is probably the so-called **leucic acid**, obtained from leucine by the action of nitrous acid.

It is crystalline, melts at 73°, and sublimes near 100°. The oxycaproic acid obtained from bromcaproic acid appears to be different. This compound melts at 60–62° (*Berichte*, 14, 1401).

(2) γ-**Oxycaproic Acid**, $CH_3.CH_2.CH(OH).CH_2.CH_2.CO_2H$, like a γ-oxy-acid, decomposes when free into water and its lactone, **Caprolactone**, $C_6H_{10}O_2$. The latter is obtained from bromcaproic acid (from hydrosorbic acid and HBr, p. 245), on heating the latter with water (*Annalen*, 208, 66), and from arabinose-carbonic acid, $C_6H_{12}O_7$, by reduction with hydriodic acid (*Berichte*, 20, 339). It is a liquid, boiling at 200°, and dissolves in 5–6 volumes H_2O at 0°. On heating, caprolactone again separates. Nitric acid oxidizes it to succinic acid.

(3) δ-**Oxycaproic Acid**, $CH_3.CH(OH).(CH_2)_3.CO_2H$, is formed from γ-aceto-butyric acid (p. 344). It furnishes a δ-lactone (p. 353), which melts at 18°, and boils at 230°. It forms a neutral solution with water, but this becomes acid after some time.

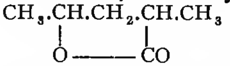
(4) γ-**Oxyisocaproic Acid**, $(CH_3)_2.C(OH).CH_2.CH_2.CO_2H$. When free, this breaks up into water and the corresponding lactone, **Isocaprolactone**, $C_6H_{10}O_2$. The latter appears in oxidizing isocaproic acid with $KMnO_4$ or HNO_3; by the distillation of terebic acid (see this), and in the transposition of pyroterebic acid (p. 241), when heated alone or with hydrobromic acid (*Annalen*, 208, 55):—



$$\underset{\text{Pyroterebic Acid.}}{(CH_3)_2C{:}CH.CH_2.CO.OH} \quad \text{yields} \quad \underset{\text{Isocaprolactone.}}{\begin{matrix}(CH_3)_2C.CH_2.CH_2\\ |\qquad\quad |\\ O\text{———}CO.\end{matrix}}$$

Isocaprolactone melts near 7°, boils at 206–207°, and is soluble in double its volume of water at 0°. When the solution is heated, it becomes turbid and the lactone separates. Dilute nitric acid oxidizes a CH_2 group in caprolactone (also in valerolactone) to carboxyl (*Berichte*, 15, 2324).

(5) **γ-Oxy-α-methylvaleric Acid,** $CH_3.CH(OH).CH_2.CH{<}\begin{matrix}CH_3\\CO_2H\end{matrix}$, and its lactone, **$\alpha$-Methylvalerolactone,** or symmetrical caprolactone,



$$\begin{matrix}CH_3.CH.CH_2.CH.CH_3\\ | \qquad\quad | \\ O\text{———}CO\end{matrix}$$

, are obtained from β-aceto-isobutyric acid (p. 344), by the action of nascent hydrogen, and by reducing saccharin, $C_6H_{10}O_5$, with hydriodic acid (*Berichte*, 16, 1821). The lactone boils at 206°, and dissolves in 20 volumes of water. Further heating with HI, changes it to methyl-propyl acetic acid (p. 230).

(6) **γ-Oxy-β-methylvaleric Acid,** $CH_3.CH(OH).CH(CH_3).CH_2.CO_2H$, and its lactone, β-methyl valerolactone, are obtained from β-aceto-butyric acid (p. 344). The lactone boils at 210°.

(7) **Oxyheptylic Acids,** $C_7H_{14}O_3$.

The **heptolactone,** $C_7H_{12}O_2$, corresponding to γ-oxyheptylic acid, is formed on reducing teracrylic acid, $C_7H_{12}O_2$ (p. 241), with hydrobromic acid, just as iso-caprolactone is obtained from pyroterebic acid (see above). Heptolactone melts at 11°, and boils at 220°. It dissolves in 12 volumes of water at 0°.

Many other higher oxy-fatty acids have been obtained from oxalic ester by means of propyl iodide, amyl iodide, etc., and zinc, and also from the higher aceto-acetic esters, by the use of sodium amalgam. The unsaturated acids, *allyl oxyacetic acid*, $C_3H_5.CH(OH).CO_2H$, and *diallyl oxyacetic acid*, $(C_3H_5)_2C(OH).CO_2H$, are produced in a similar manner.

UNSATURATED OXY-ACIDS, $C_nH_{2n-2}O_3$.

But few of this class are known.

(1) **Oxyacrylic Acid,** $C_3H_4O_3 = CH(OH){:}CH.CO_2H$, appears to form upon boiling β-chloracrylic ester with baryta. It is very unstable, and passes rapidly into malonic acid.

(2) **Oxycrotonic Acid,** $C_4H_6O_3$, is not known in a free condition. The alkylized β-oxycrotonic acids:—

$$CH_3.C(O.CH_3){:}CH.CO_2H \text{ and } CH_3.C(O.C_2H_5){:}CH.CO_2H,$$

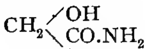
Methyloxycrotonic Acid. Ethyloxycrotonic Acid.

have been prepared from β-chlorcrotonic and chlorisocrotonic acids by the action of sodium methylate and ethylate. Both are crystalline, insoluble in water and very readily sublimed. The first melts at 128°, the second at 137°.

(3) **Oxyangelic Acid,** $C_5H_8O_3$. The lactones of the γ- and δ-oxy acids have been obtained by the distillation of lævulinic acid (p. 343).

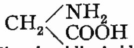
AMIDES OF THE DIHYDRIC ACIDS.

In the dihydric acids both the alcoholic and acid hydroxyl group can be replaced by the amid-group, NH_2. In the first instance *amic* or *amido-acids* result, while in the second case we get the isomeric *acid amides* (p. 255). The *imides* result by substituting the divalent acid radicals for two of the hydrogen atoms of ammonia (p. 353):—



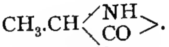
$$CH_2{<}\begin{matrix}OH\\CO.NH_2\end{matrix}$$

Glycolamide.



$$CH_2{<}\begin{matrix}NH_2\\COOH\end{matrix}$$

Glycolamidic Acid.



$$CH_3.CH{<}\begin{matrix}NH\\CO\end{matrix}{>}.$$

Lactimide.

1. Amides.

Glycolamide, $C_2H_5NO_2 = CH_2\Big\langle{}^{OH}_{CO.NH_2}$, is directly produced on heating glycolide (p. 356) with dry ammonia, or from acid ammonium tartronate when heated to 150°. It crystallizes in needles, melting at 120°, possesses a sweet taste, and dissolves easily in water, but with difficulty in alcohol. When boiled with alkalies it breaks down into glycollic acid and ammonia.

Lactamide, $C_3H_7NO_2 = CH_3.CH\Big\langle{}^{OH}_{CO.NH_2}$, is obtained by the union of lactide with ammonia, and upon heating ethyl lactic ester with ammonia. It forms crystals, readily soluble in water and alcohol, and melts at 74°. Boiling alkalies break it up into lactic acid and ammonia.

Lactimide, $C_3H_5NO = C_3H_4O{:}NH$, is produced by heating alanine, $CH_3.CH\Big\langle{}^{NH_2}_{CO_2H}$, in a current of HCl to 180–200°. It consists of colorless leaflets or needles, which melt at 275°, and dissolve readily in water and alcohol.

2. Amic or Amido-Acids.

Here the alcoholic hydroxyl is replaced by the group NH_2:—

$$\begin{array}{ccc} CH_2.OH & & CH_2.NH_2 \\ | & \text{and} & | \\ CO.OH & & CO.OH \\ \text{Glycollic Acid} & & \text{Glycolamidic Acid.} \end{array}$$

It is simpler to view them as amido-derivatives of the monobasic fatty acids, produced by the replacement of one hydrogen atom in the latter by the amido-group:—

$$\begin{array}{ccc} CH_3 & \qquad & CH_2.NH_2 \\ | & & | \\ CO.OH & & CO.OH \\ \text{Acetic Acid.} & & \text{Amidoacetic Acid.} \end{array}$$

Hence they are usually called *amido-fatty acids*. The firm union of the amido-group in them is a characteristic difference between these compounds and their isomeric acid amides. Boiling alkalies do not eliminate it (similar to the amines). Several of these amido-acids occur already formed in animal organisms. Great physiological importance attaches to them here. They have received the name *alanines* or *glycocolls* from their most important representatives.

The general methods in use for preparing the amido-acids are:—

(1) The transposition of the monohalogen fatty acids when heated with ammonia (similar to the formation of the amines from the alkylogens, p. 157):—

$$\underset{\text{Monochlor-acetic Acid.}}{CH_2Cl.CO_2H} + 2NH_3 = \underset{\text{Amido-acetic Acid.}}{CH_2(NH_2).CO_2H} + NH_4Cl.$$

(2) The reduction of nitro- and isonitroso-acids (p. 214) with nascent hydrogen (Zn and HCl):—

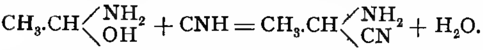
$$\underset{\beta\text{-Nitropropionic Acid.}}{CH_2(NO_2).CH_2.CO_2H} + 3H_2 = \underset{\beta\text{-Amido-propionic Acid.}}{CH_2(NH_2).CH_2.CO_2H} + 2H_2O.$$

(3) Transposition of the cyan-fatty acids (p. 262) with nascent H(Zn and HCl, or by heating with HI), in the same manner that the amines are produced from the alkyl cyanides (p. 159):—

$$\underset{\text{Cyanformic Acid.}}{CN.CO.OH} + 2H_2 = \underset{\text{Amido-acetic Acid.}}{CH_2(NH_2).CO_2H.}$$

Cyanformic acid and glycocoll are formed from dicyanogen by the same method.

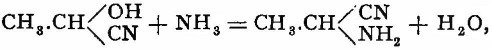
(4) A synthetic method consists in heating the aldehyde-ammonias with hydrocyanic acid and hydrochloric acid (p. 190):—



$$CH_3.CH\left\langle\begin{matrix}NH_2\\OH\end{matrix}\right. + CNH = CH_3.CH\left\langle\begin{matrix}NH_2\\CN\end{matrix}\right. + H_2O.$$

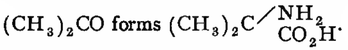
The amido acids are then obtained on boiling the products with hydrochloric acid.

A more advantageous method consists in converting the cyanides of the aldehydes (p. 190) into amid-cyanides by means of alcoholic ammonia (in equivalent quantity):—



$$CH_3.CH\left\langle\begin{matrix}OH\\CN\end{matrix}\right. + NH_3 = CH_3.CH\left\langle\begin{matrix}CN\\NH_2\end{matrix}\right. + H_2O,$$

and saponifying these with hydrochloric acid (*Berichte*, 14, 1965). In this manner the ketones can also be changed through the cyanides (p. 255) to amido-acids:—

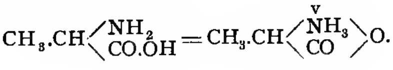


$$(CH_3)_2CO \text{ forms } (CH_3)_2C\left\langle\begin{matrix}NH_2\\CO_2H\end{matrix}\right..$$

The aldehydes, too, can be converted into amido-acids by means of ammonium cyanide (*Berichte*, 14, 2686).

(5) The conversion of the unsaturated acids upon heating them to 100° with ammonia. This seems to be a very common method. Thus, crotonic acid, by this treatment, becomes β-amido-butyric acid (p. 372). Aspartic acid results in a similar manner from fumaric and maleïc acids (*Berichte*, 21, Refs. 86 and 523).

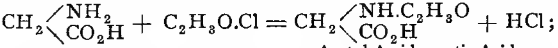
As the amido-acids contain both a carboxyl and an amido-group, they are acids and bases (amines). They yield salt-like derivatives with metallic oxides and with acids, and are capable also of directly combining with certain salts. Since, however, the carboxyl and amido-groups mutually neutralize each other, the amido-acids show neutral reaction, and it is very probable that both groups combine to produce an ammonium salt:—



$$CH_3.CH\left\langle\begin{matrix}NH_2\\CO.OH\end{matrix}\right. = CH_3.CH\left\langle\begin{matrix}\overset{v}{N}H_3\\CO\end{matrix}\right\rangle O.$$

The existence and method of producing trimethyl glycocoll or betaïne would indicate this (p. 316). A separation of the two groups would again occur in the formation of the salts.

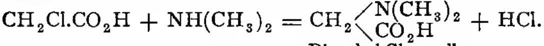
The hydrogen of the CO.OH group can be replaced by alcohol radicals with formation of *esters*, which are, however, unstable. On the other hand, the hydrogen of the amido-group can be replaced by both acid and alcohol radicals. The *acid derivatives* appear when acid chlorides act upon the amido-acids or their esters:—



$$CH_2\Big\langle\begin{matrix}NH_2\\CO_2H\end{matrix} + C_2H_3O.Cl = CH_2\Big\langle\begin{matrix}NH.C_2H_3O\\CO_2H\end{matrix} + HCl;$$

Acetyl Amido-acetic Acid.

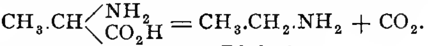
whereas the *alcohol derivatives* are obtained by the action of the amines on substituted fatty acids:—



$$CH_2Cl.CO_2H + NH(CH_3)_2 = CH_2\Big\langle\begin{matrix}N(CH_3)_2\\CO_2H\end{matrix} + HCl.$$

Dimethyl Glycocoll.

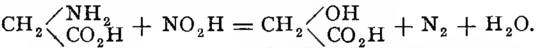
The amido-acids are crystalline bodies with usually a sweet taste, and are readily soluble in water. As a general thing, they are insoluble in alcohol and ether. Consult *Berichte*, 18, 388, upon active and inactive amido acids. They are not affected by boiling alkalies, but when fused they decompose into salts of the fatty acids and into amines or ammonia. By dry distillation (with baryta especially) they yield amines and carbon dioxide:—



$$CH_3.CH\Big\langle\begin{matrix}NH_2\\CO_2H\end{matrix} = CH_3.CH_2.NH_2 + CO_2.$$

Ethylamine.

Nitrous acid converts them into oxy-acids:—



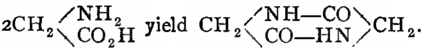
$$CH_2\Big\langle\begin{matrix}NH_2\\CO_2H\end{matrix} + NO_2H = CH_2\Big\langle\begin{matrix}OH\\CO_2H\end{matrix} + N_2 + H_2O.$$

Glycollic Acid.

When potassium nitrite is allowed to act on the hydrochlorides of the esters of the amido-acids, esters of the diazo-fatty acids (p. 373) are produced. Their formation serves as a test for even minute quantities of the amido-acids (*Berichte*, 17, 959). Ferric chloride yields a red color with all the amido-acids. Acids discharge the same.

By continuing the introduction of methyl into the amido-acids it is possible to entirely split off the amido-group. Unsaturated acids result. Thus, α-amidopropionic acid yields acrylic acid, and α-amido-butyric acid yields crotonic acid (*Berichte*, 21, Ref. 86).

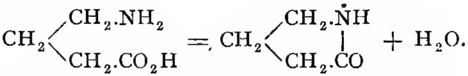
Amido-anhydrides are produced by the elimination of water from the amido-acids. They correspond to the ester anhydrides (p. 351). When this change occurs with glycocoll and glycollic acid (p. 351) two molecules unite (*Berichte*, 21, Ref. 254, and 22, 793):—



$$2CH_2\Big\langle\begin{matrix}NH_2\\CO_2H\end{matrix} \text{ yield } CH_2\Big\langle\begin{matrix}NH—CO\\CO—HN\end{matrix}\Big\rangle CH_2.$$

Glycocoll.

The γ- and δ-amido-acids are capable of forming amido-anhydrides by inner condensation. In this respect they are analogous to γ- and δ-oxy-acids. This new class of compounds has been designated *lactams* (compare the lactams of the aromatic series). They contain closed chains of five and six members. Thus, γ-amido-butyric acid yields pyrrolidon (belonging to the pyrrol series) (*Berichte*, **22**, 3338; **23**, 888):—

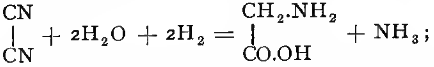


δ-Amido-valeric acid, $CH_2(NH_2).CH_2.CH_2.CH_2.CO_2H$, is similarly converted into oxy-piperidine, C_5H_9NO (or piperidon).

Taurine, described p. 319, belongs to the amido-acids.

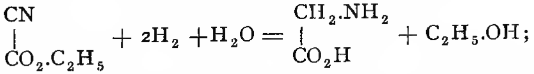
Glycocoll,	$C_2H_5NO_2$
Alanine,	$C_3H_7NO_2$
Propalanine,	$C_4H_9NO_2$
Butalanine,	$C_5H_{11}NO_2$
Leucine,	$C_6H_{13}NO_2$.

1. **Glycocoll**, Amido-acetic Acid, $C_2H_5NO_2 = CH_2(NH_2).CO_2H$, is produced in the decomposition of various animal substances, like hippuric acid, glycocholic acid or glue (hence the name glycocoll: glucus, sweet; kolla, glue), when they are boiled with alkalies or acids. It is obtained synthetically: by heating monochloracetic acid with ammonia; by conducting cyanogen gas into boiling hydriodic acid:—



$$\begin{matrix} CN \\ | \\ CN \end{matrix} + 2H_2O + 2H_2 = \begin{matrix} CH_2.NH_2 \\ | \\ CO.OH \end{matrix} + NH_3;$$

furthermore, by the action of zinc and hydrochloric acid upon cyancarbonic ester (p. 377) in alcoholic solution:—



$$\begin{matrix} CN \\ | \\ CO_2.C_2H_5 \end{matrix} + 2H_2 + H_2O = \begin{matrix} CH_2.NH_2 \\ | \\ CO_2H \end{matrix} + C_2H_5.OH;$$

and finally, by letting ammonium cyanide and sulphuric acid act upon glyoxal, CHO.CHO (p. 324), when the latter probably at first yields formaldehyde, CH_2O (*Berichte*, **15**, 3087). Alanine is analogously formed from acetaldehyde and ammonium cyanide.

In preparing glycocoll, pour 2 parts of concentrated sulphuric acid over finely divided glue (1 part), let stand several days, then add 8 parts of water and boil for some time, with occasional addition of water to replace the evaporated steam. Next, neutralize with chalk, filter and concentrate the filtrate. The glycocoll obtained in this manner is crystallized from hot, dilute alcohol, to free it of any adherent leucine.

A simpler procedure employs hippuric acid,  $CH_2\left\langle\begin{matrix}NH.C_7H_5O\\CO_2H\end{matrix}\right.$ (benzoyl glycocoll). The latter is boiled with concentrated HCl (4 parts) for about one hour, allowed to cool, the separated benzoic acid filtered off, and the filtrate concentrated. The resulting glycocoll hydrochloride is boiled with water and lead oxide, the lead chloride filtered off and the excess of Pb precipitated by H_2S. In evaporating the filtered solution glycocoll crystallizes out.

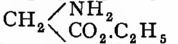
Glycocoll is also obtained by warming monochloracetic acid with dry ammonium carbonate (*Berichte*, 16, 2827).

It is most easily prepared by heating phthalylglycocoll ester, $C_8H_4O_2:N.CH_2.CO_2.C_2H_5$ (from phthalimide and chloracetic ester), to 200° with hydrochloric acid (*Berichte*, 22, 426).

Glycocoll crystallizes from water in large, rhombic prisms, which are soluble in 4 parts of cold water. It is insoluble in alcohol and ether. It possesses a sweetish taste, and melts with decomposition at 232–236°. Heated with baryta it breaks up into methylamine and carbon dioxide; nitrous acid converts it into glycollic acid. Ferric chloride imparts an intense red coloration to glycocoll solutions; acids discharge this, but ammonia restores it.

Glycocoll yields the following compounds with hydrochloric acid: $C_2H_5NO_2.HCl$ and $2(C_2H_5NO_2).HCl$. The first is obtained with an excess of hydrochloric acid. It crystallizes in long prisms. The *nitrate*, $C_2H_5NO_2.HNO_3$, forms large prisms.

An aqueous solution of glycocoll will dissolve many metallic oxides, forming salts. Of these the *copper salt*, $(C_2H_4NO_2)_2Cu + H_2O$, is very characteristic. It crystallizes in dark blue needles. The *silver salt*, $C_2H_4NO_2Ag$, crystallizes on standing over sulphuric acid. The combinations of glycocoll with salts, *e. g.*, $C_2H_5NO_2.NO_3K$, $C_2H_5NO_2.NO_3Ag$, are mostly crystalline.

The *ethyl ester*,  $CH_2\left\langle\begin{matrix}NH_2\\CO_2.C_2H_5\end{matrix}\right.$ (*Berichte*, 17, 957), is an oil with an odor resembling that of cacao, and boiling at 149°. It is very unstable and readily becomes an anhydride $(CH_2(NH)CO)_2$ (*Berichte*, 16, 755). On leading HCl gas into glycocoll and absolute alcohol, the HCl-salt is formed; this melts at 144°. The hydrochlorides of the methyl and propyl esters, etc. (*Berichte*, 21, Ref. 253), are produced in a similar manner.

Glycocoll Anhydride, $(CH_2.CO.NH)_2$ (?), forms upon evaporating glycocoll ester with water. It crystallizes from hot water in large plates. When these are rapidly heated they sublime in needles. If heated slowly, they become brown at 245° and melt at 275° (*Berichte*, 22, 793).

Glycocollamide,  $CH_2\left\langle\begin{matrix}NH_2\\CO_2NH_2\end{matrix}\right.$, amidoacetamide, is produced when glycocoll is heated with alcoholic ammonia to 160°. A white mass which dissolves readily in water, and reacts strongly alkaline. The HCl-salt results on heating chloracetic ester to 70° with alcoholic ammonia.

Methyl-glycocoll, $C_3H_7NO_2 =$  $CH_2\left\langle\begin{matrix}NH.CH_3\\CO_2H\end{matrix}\right.$, **Sarcosine**, is obtained in the action of methylamine upon monochloracetic acid (p. 368), and is also produced when creatine and caffeïne are heated with baryta. It crystallizes in rhombic prisms, which dissolve readily in water but with difficulty in alcohol. It melts at 210–220°, decomposing into carbon dioxide and dimethylamine, yielding at the same time an anhydride, $(C_3H_5NO)_2$, which melts at 150° and boils at 350°

(*Berichte*, 17, 286). It forms salts with acids; these have an acid reaction. Ignited with soda-lime it evolves methylamine. Nitrous acid changes it to the nitroso-compound, $CH_2\left\langle\begin{matrix}N(NO).CH_3\\CO_2H\end{matrix}\right.$. Sarcosine yields methylhydantoïn with cyanogen chloride.

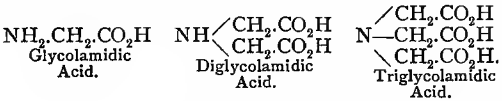
Trimethylglycocoll, $CH_2\left\langle\begin{matrix}N(CH_3)_3\\CO.O\end{matrix}\right\rangle$, is betaïne, described p. 316.

Ethyl-glycocoll, $C_4H_9NO_2 = CH_2\left\langle\begin{matrix}NH.C_2H_5\\CO_2H\end{matrix}\right.$, is obtained by heating monochloracetic acid with ethylamine. It consists of deliquescent leaflets; it unites with acids, bases and salts.

Diethyl-glycocoll, $CH_2\left\langle\begin{matrix}N(C_2H_5)_2\\CO_2H\end{matrix}\right.$, is derived from monochloracetic acid and diethylamine. It consists of deliquescent crystals which sublime under 100°.

Aceto-glycocoll, $CH_2\left\langle\begin{matrix}NH.C_2H_3O\\CO_2H\end{matrix}\right.$, aceturic acid, is obtained by the action of acetyl chloride upon glycocoll silver, and of acetamide upon monochloracetic acid. It consists of small needles, which dissolve readily in water and alcohol, and char at 130°. It conducts itself like a monobasic acid. (Compare phenyl-acetonic acid, *Berichte*, 21, Ref. 715.)

Glycocoll may be viewed as ammonia with one hydrogen atom replaced by the monovalent group, —$CH_2.CO_2H$. It is plain that two and three hydrogen atoms in NH_3 may be replaced by this group:—



$NH_2.CH_2.CO_2H$ Glycolamidic Acid.

$NH\left\langle\begin{matrix}CH_2.CO_2H\\CH_2.CO_2H\end{matrix}\right.$ Diglycolamidic Acid.

$N\left\langle\begin{matrix}CH_2.CO_2H\\CH_2.CO_2H\\CH_2.CO_2H.\end{matrix}\right.$ Triglycolamidic Acid.

These compounds are formed, together with glycocoll, on boiling monochloracetic acid with concentrated aqueous ammonia. The solution is concentrated, filtered off from the separated ammonium chloride, and boiled with lead oxide. On cooling, the lead salt of triglycolamidic acid separates out, while glycocoll and lead diglycolamidate remain dissolved. To remove the last compound, hydrogen sulphide is added to the solution, and the filtrate boiled with zinc carbonate. Zinc diglycolamidate separates out, while glycocoll remains dissolved.

Di- and triglycolamidic acids are crystalline compounds, forming salts with bases and acids; the first is dibasic, the second tribasic. Diglycolamidic acid yields a nitroso-compound with nitrous acid.

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2. *Amidopropionic Acids*, $C_3H_7NO_2 = C_3H_5(NH_2)O_2$.

(1) *α*-**Amidopropionic Acid**, $CH_3.CH(NH_2).CO_2H$, **Alanine**, is derived from *α*-chlor- and brom-propionic acid by means of ammonia, and from aldehyde ammonia by the action of CNH and HCl (p. 367). Aggregated, hard needles, with a sweetish taste. The acid dissolves in 5 parts of cold water and with more difficulty in alcohol; in ether it is insoluble. When heated it commences to char about 237°, melts at 255° and then sublimes. It is

partially decomposed into ethylamine and carbon dioxide. Nitrous acid converts it into α-lactic acid.

(2) β-**Amidopropionic Acid**, $CH_2(NH_2).CH_2.CO_2H$, is obtained from β-iodpropionic acid and β-nitropropionic acid (p. 224). It crystallizes in rhombic prisms which dissolve readily in water. When heated it melts at 180° and sublimes with partial decomposition. Its copper compound is far more soluble than that of the isomeric alanine.

3. *Amidobutyric Acids*, $C_4H_7(NH_2)O_2$.

α-**Amidobutyric Acid**, $CH_3.CH_2.CH(NH_2).CO_2H$, **Propalanine**, is obtained from brombutyric acid. It crystallizes in little leaflets or needles and is very soluble in water.

β-**Amidobutyric Acid**, $CH_3.CH(NH_2).CH_2.CO_2H$, is apparently produced when crotonic acid is heated with ammonia (p. 367).

γ-**Amidobutyric Acid**, $CH_2(NH_2).CH_2.CH_2.CO_2H$, can be obtained from phthalimide-trimethylene cyanide (*Berichte*, 22, 3337). It is very readily soluble in water. It melts at 183°, and breaks down into water and pyrrolidon (p. 369).

α-**Amidoisobutyric Acid**, $(CH_3)_2C(NH_2).CO_2H$, is made from acetonyl-urea on heating with hydrochloric acid, and is obtained from acetone by means of CNH, NH_3 and HCl (p. 367). It is also produced in the oxidation of diacetonamine with chromic acid (together with amido-isovaleric acid, p. 208). It crystallizes in large rhombic plates, and sublimes without decomposition near 220°.

4. **Amido-valeric Acids**, $C_5H_9(NH_2)O_2$.—α-**Amido-isovaleric Acid**, $CH_3.CH_2.CH_2CH(NH_2).CO_2H$, is formed on treating butyraldehyde with hydrocyanic and hydrochloric acids. It consists of shining prisms, which sublime without fusing. It is also produced by the oxidation of conine (*Berichte*, 19, 500).

γ-**Amidovaleric Acid**, $CH_3.CH(NH_2).CH_2.CH_2.CO_2H$, results from the decomposition of phenyl hydrazone-lævulinic acid (p. 343) by sodium amalgam (*Berichte*, 22, 1860). It is crystalline, melts at 193° and forms an anhydride, which is a pyrroline derivative. Boiling alkalies and baryta convert it again into the acid.

δ-**Amidovaleric Acid**, $CH_2(NH_2).(CH_2)_3.CO_2H$ (Homopiperidic Acid), is produced when piperidine is oxidized. It forms shining leaflets, melts at 158°, and breaks down into water and oxy-piperidine, C_5H_8ONH. The latter is resolved, by acids or alkalies, into the amido-acid. The latter is an indifferent compound, but oxy-piperidine is a powerful poison (*Berichte*, 21, 2235).

α-**Amido-isovaleric Acid**, $(CH_3)_2.CH.CH(NH_2).CO_2H$, **Butalanine**, occurs in the pancreas of the ox, and is produced by the action of ammonia upon bromisovaleric acid. It consists of shining prisms which sublime without fusing. It dissolves with more difficulty than leucine in water and alcohol.

β-**Amido-isovaleric Acid**, $(CH_3)_2C(NH_2).CH_2.CO_2H$, is obtained by the reduction of the nitro-acid (p. 228); it melts and sublimes at 215°.

(5) *α*-**Amido-caproic Acid**, $CH_3.(CH_2)_3.CH(NH_2).CO_2H$, **Leucine**, occurs in different animal juices, in the pancreas, and is formed by the decay of albuminoids, or when they are boiled with alkalies or acids. Artificial leucine prepared from bromcaproic acid and valeric aldehyde appears to be an isomeride of the preceding.

Leucine crystallizes in shining leaflets, which have a fatty feel, melt at 170° and sublime undecomposed when carefully heated. Rapid heating breaks it up into amylamine and CO_2. It is soluble in 48 parts of water at 12° and in 800 parts of alcohol.

The leucines derived from different sources differ in their optical behavior. The synthetic variety (from brom-caproic acid and valeric aldehyde) is inactive. Penicillium glaucum causes this variety to ferment, and it is then transformed into the lævorotatory variety. Boiling baryta water changes this again into the inactive. Therefore, when albuminoids are decomposed by boiling baryta water the product is inactive leucine. Active lævo-leucine results if the decomposition be effected with hydrochloric acid (*Berichte*, **17**, 1439; **18**, 2984).

Nitrous acid converts it into leucic acid (p. 364). Fused with potash it decomposes into ammonium and potassium valerates. When oxidized with lead peroxide we get valeronitrile, $C_5H_{11}.CN$.

DIAZO-ACIDS.

Acids of this class, like diazo-acetic acid, $CHN_2.CO_2H$, contain the diazo-group $N_2 =$, consisting of two nitrogen atoms, instead of two hydrogen atoms. They are similar to the diazo-derivatives of the aromatic series, but not wholly like them. When liberated from their salts, by mineral acids, they immediately sustain decomposition. They are rather stable when existing as esters or amides.

The esters of the diazo-acids are obtained by the action of potassium nitrite upon the hydrochlorides of the amido-fatty acid esters (p. 370) (Curtius, 1883; *Berichte*, **16**, 2230):—

$$\underset{\text{Hydrochloride of Glycocoll Ester.}}{HCl.(H_2N)CH_2.CO_2.C_2H_5} + KNO_2 = \underset{\text{Diazo-acetic Ester.}}{CH(N_2).CO_2.C_2H_5} + KCl + 2H_2O.$$

The diazo-acids are very volatile, yellow-colored liquids, with peculiar odor. They distil undecomposed with steam, or under reduced pressure. They are slightly soluble in water, but mix readily with alcohol and ether. The hydrogen of their CHN_2-group can be replaced by alkali metals. This change may be effected by the action of alcoholates. It shows that they possess a feeble acid nature. Aqueous alkalies gradually saponify and dissolve them, with the formation of salts, $CHN_2.CO_2Me$. Acids decompose these at once with the evolution of nitrogen.

Ethyl Diazoacetate, $CHN_2.CO_2.C_2H_5$, boils at 143-144° (under 120 mm. pressure); its sp. gr. is 1.073 at 22°. When chilled it solidifies, forming a leafy, crystalline mass, melting at —24°. It explodes with violence when brought in contact with concentrated sulphuric acid. A blow does not have this effect. Concentrated ammonia converts it into an amide, **diazoacetamide**, $CHN_2.CO.NH_2$, that crystallizes from water and alcohol in golden-yellow plates or prisms. The crystals become non-transparent at 112°, and melt at 114° with decomposition.

The diazo-compounds of the marsh gas series are especially reactive. They split off nitrogen, and its place is taken either by *two* monovalent atoms or radicals.

The diazo-esters are converted, by boiling water or dilute acids, into esters of the oxy-fatty acids (glycol acids):—

$$CHN_2.CO_2.C_2H_5 + H_2O = \underset{\text{Ester of Glycollic Acid.}}{CH_2(OH).CO_2.C_2H_5} + N_2.$$

This reaction can serve for the quantitative estimation of the nitrogen in diazo-derivatives. Alkyl glycollic esters are produced on boiling with alcohols:—

$$CHN_2.CO_2.C_2H_5 + C_2H_5.OH = CH_2(O.C_2H_5).CO_2.C_2H_5 + N_2;$$

a small quantity of aldehyde is produced at the same time.

Acid derivatives of the glycollic esters are obtained on heating the diazo-compounds with organic acids:—

$$CHN_2.CO_2.C_2H_5 + \underset{\text{Acetic Acid.}}{C_2H_3O.OH} = \underset{\text{Aceto-glycollic Ester.}}{CH_2(O.C_2H_3O).CO_2.C_2H_5} + N_2.$$

The haloid acids act, even in the cold, upon the diazo-compounds. The products are haloid fatty acids:—

$$CHN_2.CO_2.C_2H_5 + HCl = CH_2Cl.CO_2.C_2H_5 + N_2.$$

The halogens produce esters of dihaloid fatty acids:—

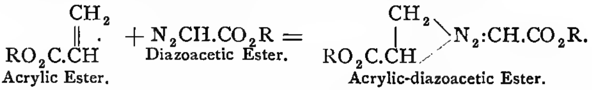
$$CHN_2.CO_2.C_2H_5 + I_2 = \underset{\text{Di-iodo-acetic Ester.}}{CHI_2.CO_2.C_2H_5} + N_2.$$

Diazo-acetamide is changed, in a similar manner, to di-iodo-acetamide, $CHI_2.CO.NH_2$. By titration with iodine it is possible to employ this reaction for the quantitative estimation of diazo-fatty compounds (*Berichte*, 18, 1285).

The esters of the diazo-fatty acids unite with aldehydes to form esters of the ketonic acids, *e. g.*, benzoylacetic ester, $C_6H_5.CO.CH_2.CO_2.C_2H_5$ (*Berichte*, 18, 1371). They produce peculiar acid esters by their union with the benzenes. These compounds are isomeric with the esters of the phenyl fatty acids (*Berichte*, 21, 2637):—

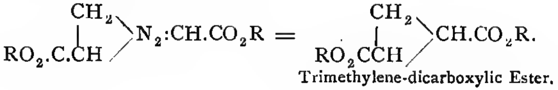
$$C_6H_6 + CHN_2.CO_2.C_2H_5 = C_6H_5.CH_2.CO_2.C_2H_5 + N_2.$$

The diazoacetic esters and the esters of the unsaturated acids (acrylic, cinnamic, fumaric) combine to additive products, which crystallize well:—



$$\underset{\text{Acrylic Ester.}}{\begin{matrix}CH_2\\ \|\\ RO_2C.CH\end{matrix}} + \underset{\text{Diazoacetic Ester.}}{N_2CH.CO_2R} = \underset{\text{Acrylic-diazoacetic Ester.}}{\begin{matrix}CH_2\\ |\\ RO_2C.CH\end{matrix}\!>\!N_2{:}CH.CO_2R.}$$

On the application of heat nitrogen is split off, and an ester of trimethylene carboxylic acid results:—



$$\begin{matrix}CH_2\\ |\\ RO_2.C.CH\end{matrix}\!>\!N_2{:}CH.CO_2R = \underset{\text{Trimethylene-dicarboxylic Ester.}}{\begin{matrix}CH_2\\ |\\ RO_2CCH\end{matrix}\!>\!CH.CO_2R.}$$

In a similar manner cinnamic ester yields phenyl-trimethylene-dicarboxylic ester, and fumaric ester, $C_2H_2(CO_2R)_2$, trimethylene-tricarboxylic ester, $C_3H_3.(CO_2R)_3$ (*Berichte*, 21, 2637; 23, 701). The compound with acetylene dicarboxylic ester (*Berichte*, 22, 842) conducts itself differently.

The esters of anilido-fatty acids result from the union of the anilines with diazo-esters. They revert to the amido-acids upon reduction (with zinc dust and glacial acetic acid). Hydrazine-fatty acids are intermediate products. These are not very stable (*Berichte*, 17, 957).

α-**Diazo-propionic Ester**, $CH_3.CN_2.CO_2.C_2H_5$, is similarly obtained from the hydrochloride of alanine ethyl ester (p. 371). It is a yellow oil. It behaves very much like diazo-acetic ester (*Berichte*, 22, Ref. 104) (see this). Diazosuccinic acid is a dibasic diazo-acid.

Triazo Compounds.

Triazo-acetic Acid (Triazo-trimethylene-tricarboxylic acid), $C_3H_3N_6(CO_2H)_3$, is formed (as sodium salt) when concentrated sodium hydroxide acts upon diazo-acetic ester. It contains three molecules of water, and crystallizes in orange-yellow, shining plates. When rapidly heated they melt at 152° (*Berichte*, 22, Ref. 133). The acid is almost insoluble in cold water, ether and benzene, but soluble in alcohol and glacial acetic acid. Its sodium salt is sparingly soluble. The *ethyl ester* melts at 110°. Ammonia converts its ester into triazo-acetamide. The acid is resolved into oxalic acid and *hydrazine* (*Berichte*, 22, Ref. 134), when digested with water or mineral acids :—

$$C_3H_3N_6(CO_2H)_3 + 6H_2O = 3C_2H_2O_4 + 3N_2H_4.$$

Consult the *Jour. pr. Chemie*, 39, 107, upon the constitution of the diazo- and triazo-derivatives (*Berichte*, 22, Ref. 196).

CARBONIC ACID AND DERIVATIVES.

The acid only exists in its salts (p. 353), and may be regarded as oxyformic acid, HO.CO.OH. Its symmetrical structure distinguishes it, however, from the other oxy-acids containing three atoms of oxygen. It is a weak *dibasic* acid and constitutes the transition to the true dibasic dicarboxylic acids—hence it will be treated separately.

Carbon Monoxide, CO, and **Carbon Dioxide**, CO_2, the anhydride of carbonic acid, have already received mention in inorganic chemistry. Paper moistened with a solution of palladious chloride is blackened by CO, hence it may be employed as a reagent for this latter compound.

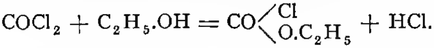
Carbonyl Chloride, $COCl_2$, Phosgene Gas, is formed by the direct union of CO with Cl_2 in sunlight (they combine very slowly in diffused light); by conducting CO into boiling $SbCl_5$, and by oxidizing chloroform (2 parts) with a mixture of concentrated sulphuric acid (50 parts) and potassium bichromate (5 parts) :—

$$2CHCl_3 + 3O = 2COCl_2 + H_2O + Cl_2.$$

The simplest course is to conduct CO and Cl_2 over pulverized and cooled bone charcoal (Paternò). Instead of condensing the gas it may be collected in cooled benzene. To remove excess of chlorine the $COCl_2$ is passed over heated antimony.

Carbonyl chloride is a colorless gas with suffocating odor, and on cooling is condensed to a liquid which boils at +8°. Water at once breaks it up into CO_2 and 2HCl.

When phosgene gas is allowed to act upon anhydrous alcohols, the esters of **chlorcarbonic acid** are formed:—

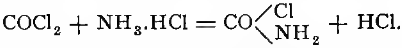


$$COCl_2 + C_2H_5.OH = CO\langle^{Cl}_{O.C_2H_5} + HCl.$$

They are more correctly termed esters of **chlorformic acid**, CClO.OH (p. 219). These are volatile, disagreeable-smelling liquids, decomposable by water. When heated with anhydrous alcohols they yield the neutral carbonic esters.

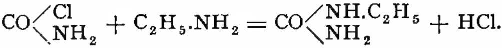
The **methyl ester**, $CClO.O.CH_3$, boils at 71.4°, the **ethyl ester**, $CClO_2.C_2H_5$, at 94°, the **propyl ester**, at 115°, the **isobutyl ester**, at 128.8°, and the **isoamyl ester**, at 154° (*Berichte*, 13, 2417).

The *amide* of chlorcarbonic acid, $CO\langle^{NH_2}_{Cl}$, called *urea chloride*, is produced by the interaction of phosgene gas and ammonium chloride at 400° (*Berichte*, 20, 858; 21, Ref. 293):—



$$COCl_2 + NH_3.HCl = CO\langle^{Cl}_{NH_2} + HCl.$$

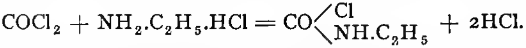
It is a liquid with penetrating odor. It solidifies in needles, which melt at 50° and boil at 61°–62°, when it dissociates into hydrochloric acid and isocyanic acid, HCNO. The latter partly polymerizes to cyamelide. Urea chloride suffers a like change on standing. Water or moist air decomposes it into carbon dioxide and ammonium chloride. It reacts violently with amines, forming substituted ureas:—



$$CO\langle^{Cl}_{NH_2} + C_2H_5.NH_2 = CO\langle^{NH.C_2H_5}_{NH_2} + HCl.$$

With the benzenes and phenol ethers it yields acid amides: $COCl.NH_2 + C_6H_6 = C_6H_5.CO.NH_2 + HCl$ (*Berichte*, 21, Ref. 214).

Alkyl Derivatives, *Alkyl Urea Chlorides*, $CO\langle^{Cl}_{NHR}$, result from the action of $COCl_2$ upon the HCl-amines at 250–270° C. (*Berichte*, 20, 118, 858; 21, Ref. 293):—



$$COCl_2 + NH_2.C_2H_5.HCl = CO\langle^{Cl}_{NH.C_2H_5} + 2HCl.$$

These are badly-smelling compounds boiling apparently without decomposition, yet they suffer dissociation into hydrochloric acid and isocyanic acid esters, CO.NR, which reunite on cooling: $CO.NR + HCl = CO\langle^{Cl}_{NHR}$. The reactions of the alkyl urea chlorides are perfectly analogous to those of urea chloride itself.

They are decomposed into CO_2 and HCl-amines by water, and with amines they yield alkylized ureas. They form carbamic and allophanic esters with alcohols (*Berichte*, 21, Ref. 293). The benzenes convert them into alkylamides of the carboxylic acids (see above). When distilled with lime they pass into isocyanic esters (see above).

Ethyl Urea Chloride, $CO\Big\langle{Cl \atop NH.C_2H_5}$, also obtained from ethylisocyanate and hydrochloric acid, boils at 60–61°. *Methyl Urea Chloride*, $CO\Big\langle{Cl \atop NH.CH_3}$, crystallizes in large leaflets, melts about 90° and boils with dissociation (see above) at 93–94°.

Dimethyl Urea Chloride, $CO\Big\langle{N(CH_3)_2 \atop Cl}$, dimethyl-carbamic chloride (p. 384), is produced by the action of dimethylamine upon $COCl_2$ dissolved in benzene. It boils at 150° C. Water decomposes it into CO_2 and dimethylamine hydrochloride.

Diethyl Urea Chloride, $CO\Big\langle{N(C_2H_5)_2 \atop Cl}$, is obtained from diethyl oxamic acid, $(C_2H_5)_2N.CO.CO_2H$, by means of PCl_5. It boils at 190–195°.

Ethyl Cyancarbonic Ester, $CO\Big\langle{CN \atop O.C_2H_5}$, or cyanformic ester, is obtained by distilling oxamic ester with P_2O_5, or better with PCl_5:—

$$\begin{array}{l}CO.NH_2\\ |\\ CO.O.C_2H_5\end{array} - H_2O = \begin{array}{l}CN\\ |\\ CO.O.C_2H_5\end{array}.$$

It is a pungent-smelling liquid, boiling at 115–116°. It is insoluble in water, but is gradually decomposed by the latter into CO_2, CNH and alcohol. Zinc and hydrochloric acid convert it into glycocoll (p. 366). Concentrated hydrochloric acid decomposes it into oxalic acid and ammonium chloride. Bromine or anhydrous HCl, at 100°, converts it into a crystalline, polymeric modification, melting at 165°, and transformed by the action of alkalies in the cold into salts of paracyancarbonic acid, *e. g.*, $(CN.CO_2K)_n$.

The *methyl ester*, $CN.CO_2.CH_3$, boils at 100–101°.

The *primary esters* of carbonic acid are not stable in a free condition. The potassium salt of **Ethyl Carbonic Acid**, $CO\Big\langle{O.C_2H_5 \atop OK}$, separates in pearly scales on adding CO_2 to the alcoholic solution of potassium alcoholate. Water decomposes it into potassium carbonate and alcohol.

The *neutral esters* appear when the alkyl iodides act on silver carbonate:—

$$CO_3Ag_2 + 2C_2H_5I = CO_3(C_2H_5)_2 + 2AgI;$$

also by treating esters of chlorformic acid with alcohols, whereby *mixed* esters may also be obtained:—

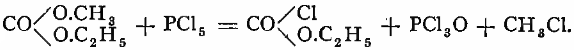
$$CO\Big\langle{Cl \atop O.CH_3} + C_2H_5.OH = \underset{\text{Methyl-ethyl Carbonate.}}{CO\Big\langle{O.C_2H_5 \atop O.CH_3}} + HCl.$$

It is also true, that, with application of heat, the higher alcohols are able to expel the lower alcohols from the mixed esters:—

$$\underset{\text{Methyl Ethyl Ester.}}{CO\Big\langle{O.C_2H_5 \atop O.CH_3}} + C_2H_5.OH = \underset{\text{Diethyl Ester.}}{CO\Big\langle{O.C_2H_5 \atop O.C_2H_5}} + CH_3OH.$$

Hence, to obtain the mixed ester, the reaction must occur at a lower temperature. As regards the nature of the product, it is immaterial as to what order is pursued in introducing the alkyl groups, *i. e.*, whether proceeding from chlorformic ester, we let ethyl alcohol act upon it, or reverse the case, letting methyl alcohol act upon ethyl chlorformic ester; the same methyl ethyl carbonic acid results in each case (*Berichte*, 13, 2417). This is an additional confirmation of the like valence of the carbon affinities, already proved by numerous experiments made with that direct object (with the mixed ketones) in view.

The neutral carbonic esters are ethereal smelling liquids, insoluble in water. Excepting dimethyl and the methyl-ethyl ester, all are lighter than water. With ammonia they first yield carbamic esters and then urea. When they are heated with phosphorus pentachloride, an alkyl group is eliminated, and in the case of the mixed esters this is always the lower one, while the chlorformic esters constitute the product:—



$$CO\left\langle\begin{matrix}O.CH_3\\O.C_2H_5\end{matrix}\right. + PCl_5 = CO\left\langle\begin{matrix}Cl\\O.C_2H_5\end{matrix}\right. + PCl_3O + CH_3Cl.$$

Methyl Carbonic Ester, $CO_3(CH_3)_2$, is produced from chlorformic ester by heating with lead oxide. It boils at 91°. The **methyl ethyl ester**, $CO_3\left\langle\begin{matrix}CH_3\\C_2H_5\end{matrix}\right.$, boils at 109°. The **ethyl ester**, $CO_3(C_2H_5)_2$, is obtained from ethyl oxalate, $C_2O_4(C_2H_5)_2$, on warming with sodium or sodium ethylate (with evolution of CO_2). It boils at 126°. The *methyl propyl ester*, $CO_3(CH_3)(C_3H_7)$, boils at 130°.

The *ethylene ester*, $CO_3C_2H_4$, glycol carbonate, obtained from glycol and $COCl_2$, melts at 39°, and boils at 236°.

Carbon mono-sulphide, analogous to carbon monoxide, is unknown.

Carbon Oxysulphide, COS, occurs in some mineral springs, and is formed in various ways, as, for example, by conducting sulphur vapor and carbon monoxide through red hot tubes. It is most easily prepared by heating potassium thiocyanate with sulphuric acid, diluted with an equal volume of water: $CN.SH + H_2O = CSO + NH_3$ (*Berichte* 20, 550).

In order to obtain it pure, conduct the gas into an alcoholic potash solution, and decompose the separated potassium ethyl thiocarbonate, $CO\left\langle\begin{matrix}O.C_2H_5\\SK\end{matrix}\right.$ (p. 382), with dilute hydrochloric acid.

Carbon oxysulphide is a colorless gas, with a faint and peculiar odor. It unites readily, and forms an explosive mixture with air. It is soluble in an equal volume of water. It is decomposed by the alkalies according to the following equation:—

$$COS + 4KOH = CO_3K_2 + K_2S + 2H_2O.$$

Thiocarbonyl Chloride, $CSCl_2$, is produced when chlorine acts upon carbon disulphide, and when the latter is heated with PCl_5 in closed tubes to 200°: $CS_2 + PCl_5 = CSCl_2 + PCl_3S$.

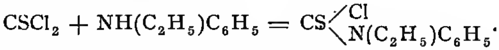
It is most readily obtained by reducing perchlormethylmercaptan, $CSCl_4$ (p. 142), with stannous chloride, or tin and hydrochloric acid (Klason, *Berichte*, 20, 2380; Billeter, 21, 102):—

$$CSCl_4 + SnCl_2 = CSCl_2 + SnCl_4.$$

This is the method employed for its production in large quantities.

It is a pungent, red-colored liquid, insoluble in water, and boiling at 73°; its sp. gr. is 1.508 at 15°. On standing exposed to sunlight, it is converted into a polymeric, crystalline compound, $C_2S_2Cl_4 = Cl.CS.S.CCl_3$, methyl perchlor-dithioformate, which melts at 116°, and at 180° reverts to the liquid body (*Berichte*, 21, 337).

Thiocarbonyl chloride converts secondary amines (1 molecule) into dialkyl sulpho-carbamic chlorides (p. 386):—



$$CSCl_2 + NH(C_2H_5)C_6H_5 = CS\begin{array}{l}\diagup Cl\\ \diagdown N(C_2H_5)C_6H_5.\end{array}$$

A second molecule of the amine produces tetra-alkylic thioureas (*Berichte*, 21, 102).

Carbon Disulphide, CS_2, is obtained by conducting sulphur vapor over ignited charcoal. It is a colorless liquid, with strong refractive power, boils at 47°, and at 0° has a specific gravity of 1.297. It is obtained pure by distilling the commercial product over mercury or mercuric chloride; its odor is then very faint. It is almost insoluble in water, but mixes with alcohol and ether. It serves as an excellent solvent for iodine, sulphur, phosphorus, fatty oils and resins. In the cold it combines with water, yielding the hydrate $2CS_2 + H_2O$, which decomposes again at —3°.

Carbon disulphide, in slight amount, is detected by its conversion into potassium xanthate. This is accomplished by means of alcoholic potash. The copper salt is obtained from the potassium compound. The production of the bright-red compound of CS_2 with triethyl phosphine (p. 169, and *Berichte*, 13, 1732) is a more delicate test.

Dry chlorine gas converts CS_2 into sulphur monochloride and thiocarbonyl chloride, $CSCl_2$. By the addition of chlorine we obtain $CSCl_4 = CCl_3.SCl$, perchlormethyl mercaptan, a yellow liquid, which becomes $CCl_3.SO_2Cl$ (p. 153) when oxidized. Zinc and hydrochloric acid convert CS_2 into trithiomethylene (p. 193).

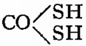
Carbon disulphide can be called the sulphanhydride of tri-thiocarbonic acid, CS_3H_2. It is perfectly analogous to CO_2, and unites with metallic sulphides, forming tri-thiocarbonates.

Tri-thiocarbonic Acid, $CS_3H_2 = CS\begin{array}{l}\diagup SH\\ \diagdown SH.\end{array}$ Hydrochloric acid precipitates this as a reddish-brown, oily liquid, from solutions of its alkali salts. The sodium salt, CS_3Na_2, separates in the form of a thick, red liquid when alcohol and ether are added to a solution of sodium sulphide containing carbon disulphide. This salt is readily dissolved by water. The barium salt, CS_3Ba, is a yellow crystalline powder, obtained by shaking aqueous BaS with CS_2.

Ethyl Trithiocarbonate, $CS\left\langle\begin{matrix}S.C_2H_5\\S.C_2H_5\end{matrix}\right.$, is formed when an alcoholic solution of ethyl iodide acts upon sodium trithiocarbonate. It is a yellow oil, insoluble in water, and boils at 240°. It forms red-colored, crystalline derivatives with two atoms of chlorine or bromine. These regenerate the ether when treated with water. The methyl ester, $CS(S.CH_3)_2$, boils at 204–205°. The action of ethylene bromide upon the sodium salt yields the *ethylene ester,* $CS\left\langle\begin{matrix}S\\S\end{matrix}\right\rangle C_2H_4$; large, yellow crystals, melting at 36.5°. These dissolve readily in ether, but with more difficulty in alcohol. When oxidized with dilute nitric acid the ester becomes ethylene-dithiocarbonic ester, $COS_2:C_2H_4$, which forms plates, melting at 31°.

Ethyl-trithiocarbonic Acid, $CS\left\langle\begin{matrix}S.C_2H_5\\SH\end{matrix}\right.$, is not known in a free condition. The *potassium salt,* $CS\left\langle\begin{matrix}S.C_2H_5\\SK\end{matrix}\right.$, is produced by the direct union of carbon-disulphide, with potassium mercaptide, $C_2H_5.SK$.

Dithiocarbonic acid, COS_2H_2, may have one of two formulas:—



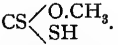
$CO\left\langle\begin{matrix}SH\\SH\end{matrix}\right.$

Dithiocarbonic Acid.

$CS\left\langle\begin{matrix}SH\\OH\end{matrix}\right.$.

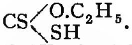
Thiosulphocarbonic Acid.*

The free acids are not known; dialkyl esters, however, do exist. Thiosulphocarbonic acid is capable of forming esters or ether acids of the type $CS\left\langle\begin{matrix}O.C_2H_5\\SH\end{matrix}\right.$, called *xanthic acids*:—



$CS\left\langle\begin{matrix}O.CH_3\\SH\end{matrix}\right.$.

Methyl Xanthate.



$CS\left\langle\begin{matrix}O.C_2H_5\\SH\end{matrix}\right.$.

Ethyl Xanthic Acid.

The esters of *dithiocarbonic acid,* $CO(SH)_2$, result when $COCl_2$ acts upon the mercaptides:—

$$COCl_2 + 2C_2H_5.SK = CO(S.C_2H_5)_2 + 2KCl;$$

and when thiocyanic esters (p. 278) are heated with concentrated sulphuric acid:—

$$2CN.S.CH_3 + 3H_2O = CO(S.CH_3)_2 + CO_2 + 2NH_3.$$

They are liquids with garlicky odor. Alcoholic ammonia decomposes them into urea and mercaptans:—

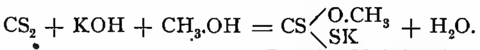
$$CO(S.C_2H_5)_2 + 2NH_3 = CO\left\langle\begin{matrix}NH_2\\NH_2\end{matrix}\right. + 2C_2H_5.SH.$$

The *methyl ester,* $CO(S.CH_3)_2$, boils at 169°; the *ethyl ester,* $CO(S.C_2H_5)_2$, at 196°.

---

* To distinguish the isomerides the sulphur joined with two valences to carbon is called *sulpho-*, the monovalent sulphur, *thio.*

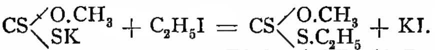
The **xanthates**, R.O.CS.SM′, are produced by the combined action of CS_2 and caustic alkalies in alcoholic solutions:—



$$CS_2 + KOH + CH_3.OH = CS\begin{array}{l}\diagup O.CH_3\\ \diagdown SK\end{array} + H_2O.$$

Potassium Methylxanthate.

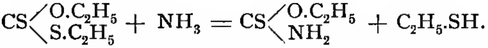
Cupric salts precipitate *yellow* copper salts from solutions of the alkaline xanthates. By the action of alkyl iodides upon the salts we obtain the esters:—



$$CS\begin{array}{l}\diagup O.CH_3\\ \diagdown SK\end{array} + C_2H_5I = CS\begin{array}{l}\diagup O.CH_3\\ \diagdown S.C_2H_5\end{array} + KI.$$

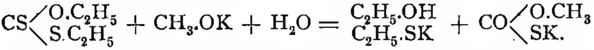
Ethyl-methyl Xanthic Ester.

The latter are liquids, not soluble in water. Ammonia breaks them up into mercaptans and esters of sulphocarbamic acid (p. 385):—



$$CS\begin{array}{l}\diagup O.C_2H_5\\ \diagdown S.C_2H_5\end{array} + NH_3 = CS\begin{array}{l}\diagup O.C_2H_5\\ \diagdown NH_2\end{array} + C_2H_5.SH.$$

With alkali alcoholates, mercaptan and alcohol separate, and salts of the alkyl thiocarbonic acids (p. 382) are formed (*Berichte*, **13**, 530):—



$$CS\begin{array}{l}\diagup O.C_2H_5\\ \diagdown S.C_2H_5\end{array} + CH_3.OK + H_2O = \begin{array}{l}C_2H_5.OH\\ C_2H_5.SK\end{array} + CO\begin{array}{l}\diagup O.CH_3\\ \diagdown SK.\end{array}$$

Xanthic Acid, or ethyl oxydithiocarbonic acid, $C_2H_5.O.CS.SH$. A heavy liquid, not soluble in water. It decomposes at 25° into alcohol and CS_2.

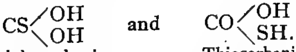
Potassium Xanthate, $C_2H_5.O.CS.SK$, forms on mixing alcoholic potash with carbon disulphide. It consists of silky needles, which dissolve very readily in water, and are quite insoluble in alcohol. The salts of the heavy metals are insoluble in water, and are obtained from the potassium salt by double decomposition. The copper salt is yellow; it decomposes on drying.

Xanthic Disulphide, $\begin{array}{l}S.CS\,O.C_2H_5\\ |\\ S.CS.O.C_2H_5\end{array}$, is produced on adding an alcoholic solution of iodine to the potassium salt (p. 251). Insoluble, shining needles, melting at 28°.

When ethyl chloride acts upon potassium xanthate, we get the *ethyl ester*, $C_2H_5.O.CS.S.C_2H_5$, a colorless oil, boiling at 200°.

The remaining alkyl oxydithiocarbonic acids are perfectly similar to xanthic acid. Ethyl-methyl xanthic ester, $CH_3O.CS.S.C_2H_5$, and methyl xanthic ester, $C_2H_5.O.CS.S.CH_3$, both boil at 184°. They are distinguished by their behavior toward ammonia and sodium alcoholate (see above).

Carbonic acid, containing one sulphur atom, may exist in two isomeric forms (p. 380):—



$$CS\begin{array}{l}\diagup OH\\ \diagdown OH\end{array} \quad \text{and} \quad CO\begin{array}{l}\diagup OH\\ \diagdown SH.\end{array}$$

Sulphocarbonic Acid. Thiocarbonic Acid.

Both acids are incapable of existing free, but they yield isomeric dialkyl esters. Thiocarbonic acid can, like xanthic acid, yield ether-thiocarbonates of the type, $CO\left\langle\begin{matrix}O.C_2H_5\\SK\end{matrix}\right.$.

Sulphocarbonic Acid. Its *ethyl ester*, $CS(O.C_2H_5)_2$, is produced by the action of sodium alcoholate upon thiocarbonyl chloride, $CSCl_2$, and in the distillation of $S_2(CS.O.C_2H_5)_2$ (see above). It is an ethereal smelling liquid, boiling at 161–162°. With alcoholic ammonia the ester decomposes into alcohol and ammonium thiocyanate, $CN.S.NH_4$; alcoholic potash converts it into alcohol and potassium ethyl thiocarbonate.

Ethyl Thiocarbonic Acid. The *potassium salt*, $CO\left\langle\begin{matrix}O.C_2H_5\\SK\end{matrix}\right.$, is obtained from xanthic esters and alcoholic potash (p. 381), and in the union of carbon dioxide with potassium mercaptide, $C_2H_5.SK$. It crystallizes in needles and prisms, which readily dissolve in water and alcohol. With ethyl iodide the potassium salt forms *ethyl thioxycarbonate*, $CO\left\langle\begin{matrix}O.C_2H_5\\S.C_2H_5\end{matrix}\right.$, which can be prepared from chlorcarbonic ester, $COCl.O.C_2H_5$, and sodium mercaptide. It boils at 156°. Alkalies decompose it into carbonate, alcohol and mercaptan. Such esters can also be prepared by acting upon the zinc mercaptides with esters of chlorcarbonic acid (*Berichte*, 19, 1228).

AMIDE DERIVATIVES OF CARBONIC ACID.

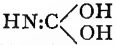
Carbonic acid is dibasic, and forms amide derivatives similar to those of the dibasic dicarboxylic acids:—

$CO\left\langle\begin{matrix}NH_2\\OH\end{matrix}\right.$

Carbamic Acid.

$CO\left\langle\begin{matrix}NH_2\\NH_2\end{matrix}\right.$

Carbamide.



$HN{:}C\left\langle\begin{matrix}OH\\OH\end{matrix}\right.$

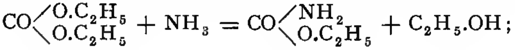
Imido-carbonic Acid.

$CO = NH$:

Carbimide.

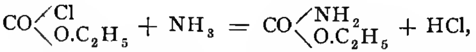
Carbamic Acid, $H_2N.CO.OH$, Amidoformic Acid, is not known in a free state. It seems its ammonium salt is contained in commercial ammonium carbonate, and is prepared by the direct union of two molecules of ammonia with carbon dioxide. It is a white mass which breaks up at 60° into $2NH_3$ and CO_2, but these combine again upon cooling. Salts of the earth and heavy metals do not precipitate the aqueous solution; it is only after warming that carbonates separate, when the carbamate has absorbed water and becomes ammonium carbonate. When ammonium carbamate is heated to 130–140° in sealed tubes, water is withdrawn and urea, $CO(NH_2)_2$, formed.

The *esters* of carbamic acid are called *urethanes;* these are obtained by the action of ammonia at ordinary temperatures upon carbonic esters:—

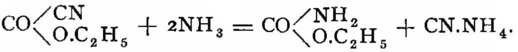


$$CO\left\langle\begin{matrix}O.C_2H_5\\O.C_2H_5\end{matrix}\right. + NH_3 = CO\left\langle\begin{matrix}NH_2\\O.C_2H_5\end{matrix}\right. + C_2H_5.OH;$$

and in the same manner from the esters of chlorcarbonic and cyancarbonic acids :—

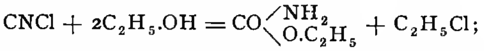


$$\mathrm{CO}\left\langle\begin{array}{l}\mathrm{Cl}\\ \mathrm{O.C_2H_5}\end{array}\right. + \mathrm{NH_3} = \mathrm{CO}\left\langle\begin{array}{l}\mathrm{NH_2}\\ \mathrm{O.C_2H_5}\end{array}\right. + \mathrm{HCl},$$



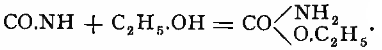
$$\mathrm{CO}\left\langle\begin{array}{l}\mathrm{CN}\\ \mathrm{O.C_2H_5}\end{array}\right. + 2\mathrm{NH_3} = \mathrm{CO}\left\langle\begin{array}{l}\mathrm{NH_2}\\ \mathrm{O.C_2H_5}\end{array}\right. + \mathrm{CN.NH_4}.$$

Also by conducting cyanchloride into the alcohols :—



$$\mathrm{CNCl} + 2\mathrm{C_2H_5.OH} = \mathrm{CO}\left\langle\begin{array}{l}\mathrm{NH_2}\\ \mathrm{O.C_2H_5}\end{array}\right. + \mathrm{C_2H_5Cl};$$

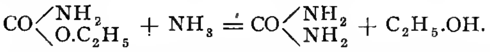
and by the direct union of cyanic acid with the alcohols :—



$$\mathrm{CO.NH} + \mathrm{C_2H_5.OH} = \mathrm{CO}\left\langle\begin{array}{l}\mathrm{NH_2}\\ \mathrm{O.C_2H_5}\end{array}\right..$$

When there is an excess of cyanic acid employed, allophanic esters are also produced.

The urethanes are crystalline, volatile bodies, soluble in alcohol, ether and water. Alkalies decompose them into CO_2, ammonia and alcohols. They yield urea when heated with ammonia :—

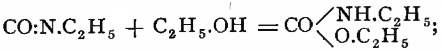


$$\mathrm{CO}\left\langle\begin{array}{l}\mathrm{NH_2}\\ \mathrm{O.C_2H_5}\end{array}\right. + \mathrm{NH_3} = \mathrm{CO}\left\langle\begin{array}{l}\mathrm{NH_2}\\ \mathrm{NH_2}\end{array}\right. + \mathrm{C_2H_5.OH}.$$

Conversely, on heating urea or its nitrate with alcohols, the urethanes are regenerated.

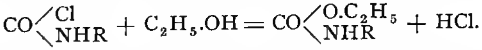
Methyl Carbamic Ester, $\mathrm{CO}\left\langle\begin{array}{l}\mathrm{NH_2}\\ \mathrm{O.CH_3}\end{array}\right.$, *methyl urethane*, crystallizes in plates, which melt at 52°, and boil at 177°. The *ethyl ester*, $CO(NH_2).O.C_2H_5$, also called urethane, consists of large plates, which melt at 47–50°, and boil at 180°. The *propyl ester* melts at 53°, and boils at 195°. The *isoamyl ester* crystallizes from water in silky needles, which melt at 60°, and boil at 220°. The *allyl ester*, $CO(NH_2).O.C_3H_5$, is a solid, melting at 21°, and boiling at 204°.

Alcohol radicals can replace the hydrogen of NH_2 in carbamic acid. The esters of these alkylized carbamic acids are formed, like the urethanes, by the action of carbonic or chlorcarbonic esters upon amines; and on heating isocyanic esters (p. 274) with the alcohols to 100° :—



$$\mathrm{CO{:}N.C_2H_5} + \mathrm{C_2H_5.OH} = \mathrm{CO}\left\langle\begin{array}{l}\mathrm{NH.C_2H_5}\\ \mathrm{O.C_2H_5}\end{array}\right.;$$

also, by the interaction of the chlorides of alkyl urea and the alcohols :—



$$\mathrm{CO}\left\langle\begin{array}{l}\mathrm{Cl}\\ \mathrm{NHR}\end{array}\right. + \mathrm{C_2H_5.OH} = \mathrm{CO}\left\langle\begin{array}{l}\mathrm{O.C_2H_5}\\ \mathrm{NHR}\end{array}\right. + \mathrm{HCl}.$$

Methyl Etho-carbamic Ester, $CH_3.HN.CO.O.C_2H_5$, boils at 170°.

Ethyl Etho-carbamic Ester, $(C_2H_5)HN.CO.O.C_2H_5$, boils at 175°.

Derivatives of carbamic acid with *divalent* radicals are produced by the union of esters of the acid with aldehydes:—

Ethidene Urethane, $CH_3.CH(HN.CO.O.C_2H_5)_2$, from urethane and acetaldehyde, crystallizes in shining needles, melting at 126° C.

Chloral Urethane, $CCl_3.CH.\left\langle\begin{matrix}OH\\HN.CO.O.C_2H_5\end{matrix}\right.$, from urethane and chloral, melts at 103°.

Cyanamido-carbonic Acid, $CO\left\langle\begin{matrix}NH.CN\\OH\end{matrix}\right.$, **Cyancarbamic acid.** Its salts are formed by the addition of CO_2 to salts of cyanamide:—

$$2CN.NHNa + CO_2 = CO\left\langle\begin{matrix}N(Na).CN\\ONa\end{matrix}\right. + CN.NH_2.$$

The *esters* of this acid result by the action of alcoholic potash upon esters of *cyanamido-dicarbonic acid*, $CN.N\left\langle\begin{matrix}CO.C_2H_5\\CO.C_2H_5\end{matrix}\right.$. The latter are produced by allowing the esters of chlorcarbonic acid to react with sodium cyanamide (*Jour. pr. Chem.*, 16, 146). The *chloride* of carbamic acid, $CO\left\langle\begin{matrix}NH_2\\Cl\end{matrix}\right.$, has been described as the *amide* of chlorcarbonic acid (p. 376). Its alkylic derivatives, or alkyl urea chlorides (p. 376) may also be termed *alkyl carbamic acid chlorides.*

Imido-carbonic Acid, $HN:C\left\langle\begin{matrix}OH\\OH\end{matrix}\right.$.

The esters of this acid are obtained by reducing the esters of chlorimido-carbonic acid (see above) with potassium arsenite. They are alkaline liquids, with ammoniacal odor, miscible with water, and again separated upon the addition of caustic alkalies. They are very unstable, distil with decomposition, and are decomposed by acids into ammonia and esters of carbonic acid. They give off the odor of carbylamine, $CN.C_2H_5$, when heated with zinc dust. They unite with amide derivatives and at the same time split off the imide group.

Their combinations with orthophenylene-diamines and ortho-amido-phenols (*Berichte*, 19, 862 and 2650) are quite interesting.

The esters of *Chlorimido-carbonic Acid*, $ClN:C\left\langle\begin{matrix}O.C_2H_5\\O.C_2H_5\end{matrix}\right.$, are produced in the action of esters of hypochlorous acid (p. 155) upon a concentrated potassium cyanide solution. They are solids, with a peculiar penetrating odor, and distil with decomposition. Alkalies have little effect upon them, while acids break them up quite easily, forming ammonia, esters of carbonic acid and nitrogen chloride.

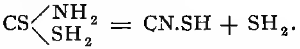
The *ethyl ester*, $ClN:C(O.C_2H_5)_2$, melts at 39°, and the *methyl ester*, $ClN:C(O.C_2H_5)_2$, at 20°.

The *chlorides* of dialkylic sulpho-carbamic acids, $CS\left\langle\begin{matrix}NR_2\\Cl\end{matrix}\right.$, are produced by the action of thiophosgene upon secondary amines (p. 378).

Cyanic acid (p. 271) is probably the imide of carbonic acid—**Carbimide**, CO:NH.

Perfectly analogous amides are derived from the thio-carbonic acids.

Dithiocarbamic Acid, $CS\left\langle\begin{matrix}NH_2\\SH\end{matrix}\right.$, is a reddish oil, obtained by decomposing the ammonium salt with dilute sulphuric acid. It breaks up very readily into thiocyanic acid and hydrogen sulphide:—

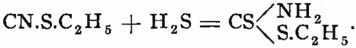


$$CS\left\langle\begin{matrix}NH_2\\SH_2\end{matrix}\right. = CN.SH + SH_2.$$

Water decomposes it into cyanic acid and $2SH_2$. The *ammonium salt* $CS\left\langle\begin{matrix}NH_2\\S.NH_4\end{matrix}\right.$, forms yellow needles or prisms, and is produced in the action of alcoholic ammonia upon CS_2.

By heating this salt together with aldehyde we obtain the compound, $H_2N.CS.S.N(CH_3.CH)_2 = C_5H_{10}S_2N_2$, *carbothialdine*. This is also obtained on mixing CS_2 with alcoholic aldehyde-ammonia (*Berichte*, 11, 1384). It consists of large, shining crystals, and when boiled with acids decomposes into ammonia, carbon disulphide and aldehyde.

The **dithiourethanes** are the esters of the above acid. They arise when the thiocyanic esters are heated with H_2S (compare phenyl dithiocarbamic acid):—

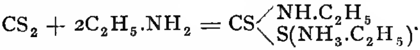


$$CN.S.C_2H_5 + H_2S = CS\left\langle\begin{matrix}NH_2\\S.C_2H_5\end{matrix}\right..$$

They are crystalline compounds, soluble in alcohol and ether, and are decomposed into ammonium thiocyanate and mercaptans, when treated with alcoholic ammonia.

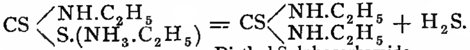
The *ethyl ester* melts at 41–42° and the *propyl ester* at 97°. Both crystallize in shining leaflets.

Alkyls may replace hydrogen of NH_2 in dithiocarbamic acid. The amine salts of these compounds are obtained on heating CS_2 with alcoholic solutions of the primary and secondary amines:—



$$CS_2 + 2C_2H_5.NH_2 = CS\left\langle\begin{matrix}NH.C_2H_5\\S(NH_3.C_2H_5)\end{matrix}\right..$$

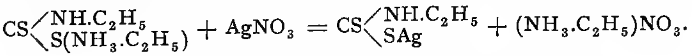
Boiling aqueous soda eliminates ethylamine from this salt and produces sodium ethyl dithiocarbamic acid, $CS\left\langle\begin{matrix}NH.C_2H_5\\SNa\end{matrix}\right.$. The free acid obtained from this is an oil which solidifies to a crystalline mass. When its amine salts are heated to 110°, dialkylic thio-ureas are produced (p. 395):—



$$CS\left\langle\begin{matrix}NH.C_2H_5\\S.(NH_3.C_2H_5)\end{matrix}\right. = CS\left\langle\begin{matrix}NH.C_2H_5\\NH.C_2H_5\end{matrix}\right. + H_2S.$$

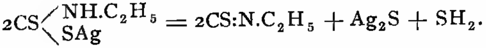
Diethyl Sulphocarbamide.

If the aqueous solution of the salts obtained from the primary amines be digested with metallic salts, *e.g.*, $AgNO_3$, $FeCl_3$ or $HgCl_2$, salts of ethyl-dithiocarbamic acid are precipitated:—



$$CS\left\langle\begin{matrix}NH.C_2H_5\\S(NH_3.C_2H_5)\end{matrix}\right. + AgNO_3 = CS\left\langle\begin{matrix}NH.C_2H_5\\SAg\end{matrix}\right. + (NH_3.C_2H_5)NO_3.$$

These yield the mustard oils when boiled with water (p. 279):—



$$2CS\left\langle\begin{matrix}NH.C_2H_5\\SAg\end{matrix}\right. = 2CS:N.C_2H_5 + Ag_2S + SH_2.$$

The salts obtained from the secondary amines do not yield mustard oils (*Berichte*, 8, 107).

Monosulphur carbamic acid can occur in two isomeric forms in its esters:—

$$\mathrm{CS}\begin{matrix}\diagup \mathrm{NH_2}\\ \diagdown \mathrm{O.C_2H_5}\end{matrix}$$

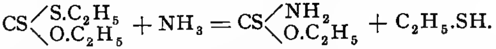
Sulphocarbamic Ester.

and

$$\mathrm{CO}\begin{matrix}\diagup \mathrm{NH_2}\\ \diagdown \mathrm{S.C_2H_5}\end{matrix}.$$

Thiocarbamic Ester.*

(1) The esters of **sulphocarbamic acid**—thiourethanes—are formed when alcoholic ammonia acts upon the xanthic esters (p. 381):—

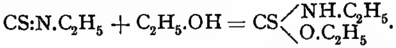


$$\mathrm{CS}\begin{matrix}\diagup \mathrm{S.C_2H_5}\\ \diagdown \mathrm{O.C_2H_5}\end{matrix} + \mathrm{NH_3} = \mathrm{CS}\begin{matrix}\diagup \mathrm{NH_2}\\ \diagdown \mathrm{O.C_2H_5}\end{matrix} + \mathrm{C_2H_5.SH}.$$

They are crystalline compounds, which decompose into mercaptans, cyanic acid and cyanuric acid on heating. Alcoholic alkalies decompose them into alcohols and thiocyanates, CNSK.

The *ethyl ester* of sulphocarbamic acid is slightly soluble in water and melts at 38°. The *methyl ester* melts at 43°.

The esters of *alkylic* sulphocarbamic acids are obtained when the mustard oils are heated to 110° with anhydrous alcohols:—

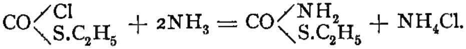


$$\mathrm{CS{:}N.C_2H_5} + \mathrm{C_2H_5.OH} = \mathrm{CS}\begin{matrix}\diagup \mathrm{NH.C_2H_5}\\ \diagdown \mathrm{O.C_2H_5}\end{matrix}.$$

They are liquids with an odor like that of leeks, boil without decomposition and break up into alcohols, CO_2, H_2S and alkylamines, when acted upon with alkalies or acids.

Ethyl Etho-sulphocarbamic Ester, $C_2H_5.NH.CS.O.C_2H_5$, boils at 204–208°. *Allyl sulphocarbamic ester*, $C_3H_5.NH.CS.O.C_2H_5$, from allyl mustard oil, boils at 210–215°.

(2) The esters of **thiocarbamic acid** are obtained by conducting hydrochloric acid gas into a solution of CNSK (or of alkyl sulphocyanates, *Berichte*, 19, 1083) in alcohols (together with esters of sulphocarbamic acid—*Journ. pract. Chem.*, 16, 358); and by the action of ammonia upon the dithiocarbonic esters, $CO(S.C_2H_5)_2$, and chlorthioformic esters:—



$$\mathrm{CO}\begin{matrix}\diagup \mathrm{Cl}\\ \diagdown \mathrm{S.C_2H_5}\end{matrix} + 2\mathrm{NH_3} = \mathrm{CO}\begin{matrix}\diagup \mathrm{NH_2}\\ \diagdown \mathrm{S.C_2H_5}\end{matrix} + \mathrm{NH_4Cl}.$$

These are crystalline compounds, which are dissolved with difficulty in water, and decompose when heated.

The *methyl ester*, $NH_2.CO.S.CH_3$, melts at 95–98°. The *ethyl ester* melts at 108°(102°).

Ammonium Thiocarbonate, $\mathrm{CO}\begin{smallmatrix}\diagup \mathrm{NH_2}\\ \diagdown \mathrm{S.NH_4}\end{smallmatrix}$, is prepared by leading COS into alcoholic ammonia. It is a colorless, crystalline mass, which acquires a yellow color on exposure to the air, owing to the formation of ammonium sulphide. When heated to 130° it breaks up into hydrogen sulphide and urea.

Carbamide, Urea, $CH_4N_2O = \mathrm{CO}\begin{smallmatrix}\diagup \mathrm{NH_2}\\ \diagdown \mathrm{NH_2}\end{smallmatrix}$.

This was discovered in urine in 1773, and was first synthesized by Wöhler in 1828. It occurs in various animal fluids, chiefly in

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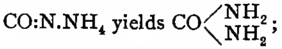
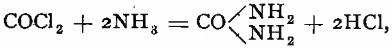
* Imidothiocarbonic acid, $\mathrm{HN{:}C}\begin{smallmatrix}\diagup \mathrm{OH}\\ \diagdown \mathrm{SH}\end{smallmatrix}$, is isomeric with these acids. It is only known in its phenyl derivatives (see phenyl isothiourethane).

the urine of mammals, birds, and some reptiles. It may be prepared artificially in various ways: (1) by evaporating the aqueous solution of ammonium isocyanate, when an atomic transposition occurs (Wöhler):—

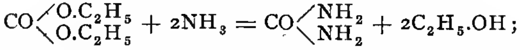


$$\mathrm{CO{:}N.NH_4}\text{ yields }\mathrm{CO}\begin{array}{l}\diagup \mathrm{NH_2}\\ \diagdown \mathrm{NH_2}\end{array};$$

(2) by the action of ammonia upon carbonyl chloride or carbonic esters:—

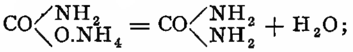


$$\mathrm{COCl_2} + 2\mathrm{NH_3} = \mathrm{CO}\begin{array}{l}\diagup \mathrm{NH_2}\\ \diagdown \mathrm{NH_2}\end{array} + 2\mathrm{HCl},$$



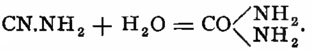
$$\mathrm{CO}\begin{array}{l}\diagup \mathrm{O.C_2H_5}\\ \diagdown \mathrm{O.C_2H_5}\end{array} + 2\mathrm{NH_3} = \mathrm{CO}\begin{array}{l}\diagup \mathrm{NH_2}\\ \diagdown \mathrm{NH_2}\end{array} + 2\mathrm{C_2H_5.OH};$$

(3) by heating ammonium carbamate or thiocarbamate to 130–140°:—



$$\mathrm{CO}\begin{array}{l}\diagup \mathrm{NH_2}\\ \diagdown \mathrm{O.NH_4}\end{array} = \mathrm{CO}\begin{array}{l}\diagup \mathrm{NH_2}\\ \diagdown \mathrm{NH_2}\end{array} + \mathrm{H_2O};$$

It is further produced in the action of alkalies upon creatine and allantoïn; in the oxidation of uric acid, guanine and xanthine, and when small quantities of acids act upon cyanamide (p. 288):—



$$\mathrm{CN.NH_2} + \mathrm{H_2O} = \mathrm{CO}\begin{array}{l}\diagup \mathrm{NH_2}\\ \diagdown \mathrm{NH_2}\end{array}.$$

Preparation from Urine. Urine is evaporated to a thick syrup, and when cool concentrated nitric acid (or, better, oxalic acid) is poured over it. The separated, brown-colored nitrate is repeatedly crystallized from dilute nitric acid, in order to obtain it pure; it is then dissolved in water, heated with barium carbonate, and the filtrate evaporated to dryness. The urea is extracted from the residue with absolute alcohol.

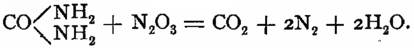
The best *synthetic* method is its preparation from ammonium cyanate. Mixed aqueous solutions of potassium cyanate and ammonium sulphate (in equivalent quantities) are evaporated; on cooling potassium sulphate crystallizes out and is filtered off, the filtrate being evaporated to dryness, and the urea extracted by means of hot alcohol. The following gives good practical results: 28 parts of anhydrous yellow prussiate of potash are fused with 14 parts of manganese dioxide. The fused mass is dissolved in water, 20½ parts of ammonium sulphate are added, and the entire solution is then evaporated to dryness. The urea is extracted from the residue with alcohol.

The easiest course to pursue in order to obtain the urea is to conduct ammonia into fused phenyl carbonate, $\mathrm{CO(O.C_6H_5)_2}$ (*Berichte*, 17, 1286).

Urea crystallizes in long, rhombic prisms or needles, which have a cooling taste, like that of saltpetre. It dissolves in 1 part of cold water and in 5 parts of alcohol; it is almost insoluble in ether. It melts at 132°, and above that temperature breaks up into ammonia, ammelide, biuret and cyanuric acid. When urea is heated above 100° with water, or when boiled with alkalies or acids, it decomposes into its constituents:—

$$\mathrm{CO{:}N_2H_4} + \mathrm{H_2O} = \mathrm{CO_2} + 2\mathrm{NH_3}.$$

Nitrous acid decomposes urea, in the same manner that it decomposes all other amides:—



$$CO\begin{matrix}\diagup NH_2\\ \diagdown NH_2\end{matrix} + N_2O_3 = CO_2 + 2N_2 + 2H_2O.$$

Urea, like glycocoll, forms crystalline compounds with acids, bases and salts. Although it is a diamide it combines with but one equivalent of acid (one of the amido-groups is neutralized by the carbonyl group).

Urea Nitrate, $CH_4N_2O.HNO_3$, crystallizes in shining leaflets, which are not very soluble in nitric acid. The *HCl-salt*, $CH_4N_2O.HCl$, is formed when dry HCl-gas is conducted over urea; it is a yellow oil, decomposing on exposure to the air. The *oxalate*, $(CH_4N_2O)_2C_2H_2O_4 + 2H_2O$, is precipitated by oxalic acid from an aqueous solution of urea in the form of thin leaflets, which are not readily soluble in water.

The compound with mercuric oxide, $CH_4N_2O.2HgO$, is a white precipitate, obtained on adding potassium hydroxide and mercuric nitrate, $Hg(NO_3)_2$, to a urea solution. *Mercuric chloride* produces a white precipitate, which assumes a yellow color when washed with water, and has then the composition expressed by the formula, $CH_4N_2O.3HgO$. Silver oxide yields a crystalline, gray compound, $(CH_4N_2O)_2.3Ag_2O$.

On evaporating a solution containing both urea and sodium chloride, the compound, $CH_4N_2O.NaCl + H_2O$, separates in shining prisms. Large rhombic prisms of $CH_4N_2O.AgNO_3$ crystallize from a concentrated solution of urea and silver nitrate.

Mercuric nitrate precipitates compounds of variable composition from aqueous urea; a volumetric method for estimating the latter is founded on this fact.

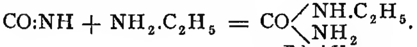
Isuretine, $CH\begin{matrix}\diagup NH_2\\ \diagdown N.OH\end{matrix}$, is isomeric with urea; it is produced by the direct union of hydroxylamine, NH_3O, with CNH (p. 294).

Hydroxy-urea, $CO\begin{matrix}\diagup NH.OH\\ \diagdown NH_2\end{matrix}$, is obtained by mixing aqueous hydroxylamine nitrate with potassium isocyanate. It is readily soluble in water and alcohol, but is thrown out of these solutions in rhombic leaflets by ether. It melts at 128–130°.

COMPOUND UREAS.

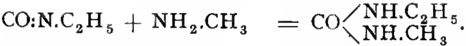
By this term we designate all compounds derived from urea by the replacement of hydrogen in the amido-groups by alcohol or acid radicals.

1. *Alkylic* ureas are produced according to the same reactions which yield urea, substituting, however, amine bases for ammonia or isocyanic esters for cyanic acid:—



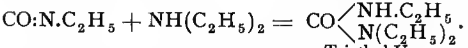
$$CO{:}NH + NH_2.C_2H_5 = CO\begin{matrix}\diagup NH.C_2H_5\\ \diagdown NH_2\end{matrix}.$$

Ethyl Urea.



$$CO:N.C_2H_5 + NH_2.CH_3 = CO\left\langle\begin{matrix}NH.C_2H_5\\NH.CH_3\end{matrix}\right..$$

Methyl-ethyl Urea.



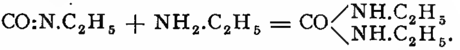
$$CO:N.C_2H_5 + NH(C_2H_5)_2 = CO\left\langle\begin{matrix}NH.C_2H_5\\N(C_2H_5)_2\end{matrix}\right..$$

Triethyl Urea.

This is the reaction with the primary and secondary amines, but not with the tertiary amines.

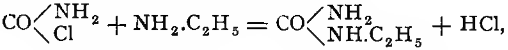
Alkylic ureas are formed, too, when isocyanic esters are heated with water—CO_2, and amines being produced; the latter unite with the esters:—

$$CO:N.C_2H_5 + H_2O = NH_2.C_2H_5 + CO_2 \text{ and}$$

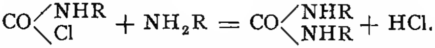


$$CO:N.C_2H_5 + NH_2.C_2H_5 = CO\left\langle\begin{matrix}NH.C_2H_5\\NH.C_2H_5\end{matrix}\right..$$

They are also obtained by the action of urea chloride and alkylurea chlorides (p. 376) upon amines:—

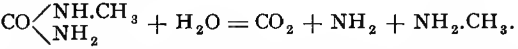


$$CO\left\langle\begin{matrix}NH_2\\Cl\end{matrix}\right. + NH_2.C_2H_5 = CO\left\langle\begin{matrix}NH_2\\NH.C_2H_5\end{matrix}\right. + HCl,$$



$$CO\left\langle\begin{matrix}NHR\\Cl\end{matrix}\right. + NH_2R = CO\left\langle\begin{matrix}NHR\\NHR\end{matrix}\right. + HCl.$$

Ureas of this class are perfectly analogous to ordinary urea so far as properties and reactions are concerned. They generally form salts with one equivalent of acid. They are crystalline salts, with the exception of those containing four alkyl groups. On heating those with one alkyl group, cyanic acid (or cyanuric acid) and an amine are produced. The higher alkylized members can be distilled without decomposition. Boiling alkalies convert them all into CO_2 and amines:—



$$CO\left\langle\begin{matrix}NH.CH_3\\NH_2\end{matrix}\right. + H_2O = CO_2 + NH_2 + NH_2.CH_3.$$

Methyl Urea, $CO\left\langle\begin{matrix}NH.CH_3\\NH_2\end{matrix}\right.$, results on heating methyl aceto-urea (from acetamide by the action of bromine and caustic potash, p. 391 and *Berichte*, 15, 409) with potassium hydroxide (*Berichte*, 14, 2734). It consists of prisms melting at 102°. Sodium nitrite converts its nitrate into **nitroso-methyl** urea, $CO(NH_2).N(NO).CH_3$. By reduction this yields methylhydrazine (p. 167).

Ethyl Urea, $CO\left\langle\begin{matrix}NH.C_2H_5\\NH_2\end{matrix}\right.$, forms large prisms, melting at 92°. They dissolve readily in water and alcohol. Nitric acid does not throw them out of aqueous solution.

a-**Diethyl Urea,** $CO\left\langle\begin{matrix}NH.C_2H_5\\NH.C_2H_5\end{matrix}\right.$, crystallizes in long prisms, melting at 112°, and boiling undecomposed at 263°. Nitrous acid (or KNO_2 upon the sulphate) changes it to *nitrosodiethyl urea*, $CO\left\langle\begin{matrix}NH.C_2H_5\\N(NO).C_2H_5\end{matrix}\right.$. This is a yellow oil, that solidifies on cooling, and melts at + 5°. By reduction, it yields an amido-derivative, which breaks up into CO_2, ethylamine, and ethyl hydrazine (p. 167).

β-Diethyl Urea, $\Big\langle\begin{smallmatrix}NH_2\\ N(C_2H_5)_2\end{smallmatrix}$, is formed when potassium cyanate acts upon diethylamine sulphate. Colorless crystals, melting at 70°.

Triethyl Urea, $CO\Big\langle\begin{smallmatrix}NH.C_2H_5\\ N(C_2H_5)_2\end{smallmatrix}$, melts at 63°, and distils at 223°; it is very soluble in water, alcohol and ether.

Tetraethyl Urea, $CO\Big\langle\begin{smallmatrix}N(C_2H_5)_2\\ N(C_2H_5)_2\end{smallmatrix}$, is produced on conducting $COCl_2$ into a solution of diethylamine in benzene:—

$$COCl_2 + 2NH(C_2H_5)_2 = CO\Big\langle\begin{smallmatrix}N(C_2H_5)_2\\ N(C_2H_5)_2\end{smallmatrix} + 2HCl.$$

This liquid boils at 210–215°, and has an odor resembling that of peppermint. It is soluble in acids, but is reprecipitated by alkalies.

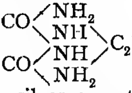
Allyl Urea, $CO\Big\langle\begin{smallmatrix}NH.C_3H_5\\ NH_2\end{smallmatrix}$, is obtained from allyl cyanic ester and ammonia, or from allylamine sulphate and potassium cyanate. It consists of beautiful prisms, melting at 85°.

Diallyl Urea, $CO\Big\langle\begin{smallmatrix}NH.C_3H_5\\ NH.C_3H_5\end{smallmatrix}$, *Sinapoline*, is formed when allyl isocyanic ester is heated with water (p. 389):—

$$2CO{:}N.C_3H_5 + H_2O = CO\Big\langle\begin{smallmatrix}NH.C_3H_5\\ NH.C_3H_5\end{smallmatrix} + CO_2;$$

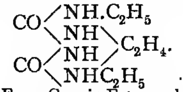
or by heating mustard oil with water and lead oxide. Diallyl-thio-urea is first formed, but the lead oxide desulphurizes it (p. 395). Diallyl-urea crystallizes in large, brilliant leaflets, melting at 100°. They do not dissolve readily in water, and have an alkaline reaction.

Ethylene Urea, $CO\Big\langle\begin{smallmatrix}NH\\ NH\end{smallmatrix}\Big\rangle C_2H_4$, is produced on heating ethyl carbonate to 180°, together with ethylene-diamine. Needles, melting at 131°, and readily soluble in both water and hot alcohol.



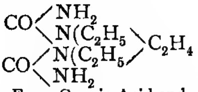
Ethylene Diurea, $\begin{smallmatrix}CO\Big\langle\begin{smallmatrix}NH_2\\ NH\end{smallmatrix}\\ CO\Big\langle\begin{smallmatrix}NH\\ NH_2\end{smallmatrix}\end{smallmatrix}\Big\rangle C_2H_4$, is produced upon heating ethylene diamine hydrochloride with silver cyanate. It dissolves with difficulty in alcohol, but readily in hot water. It melts at 192°, with decomposition.

Ethylated ethylene ureas are similarly formed:—



$$\begin{smallmatrix}CO\Big\langle\begin{smallmatrix}NH.C_2H_5\\ NH\end{smallmatrix}\\ CO\Big\langle\begin{smallmatrix}NH\\ NHC_2H_5\end{smallmatrix}\end{smallmatrix}\Big\rangle C_2H_4.$$

From Cyanic Ester and Ethylene Diamine.



$$\begin{smallmatrix}CO\Big\langle\begin{smallmatrix}NH_2\\ N(C_2H_5\end{smallmatrix}\\ CO\Big\langle\begin{smallmatrix}N(C_2H_5\\ NH_2\end{smallmatrix}\end{smallmatrix}\Big\rangle C_2H_4$$

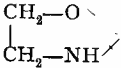
From Cyanic Acid and Diethyl Ethylene Diamine.

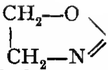
Derivatives of urea with *aldehyde radicals* exist. They are produced at ordinary temperatures by the union of urea with aldehydes; water is eliminated (*Berichte*, 22, Ref. 579).

Methylene Urea, $CO\Big\langle\begin{smallmatrix}NH\\ NH\end{smallmatrix}\Big\rangle CH_2$, is formed from urea and concentrated formic aldehyde. White, granular crystals.

Ethidene Urea, $CO\Big\langle\begin{smallmatrix}NH\\ NH\end{smallmatrix}\Big\rangle CH.CH_3$, is not very soluble in water, and melts at 154°. **Chloral Urea,** $CO(NH)_2{:}CH.CCl_3$, crystallizes in leaflets, which melt at 150° with decomposition.

When boiled with water these compounds break up into aldehydes and urea.





Ethylene-pseudo(iso)-Urea, $\begin{matrix} CH_2-O \\ | \\ CH_2-NH \end{matrix}\!\!>\!C{:}NH$, or $\begin{matrix} CH_2-O \\ | \\ CH_2-N \end{matrix}\!\!\gg\!C.NH_2$, is isomeric with ethylene urea. It is a derivative of hypothetical iso- or pseudo-urea, $HO.C\!<\!\begin{smallmatrix} NH_2 \\ NH \end{smallmatrix}$ (compare isothiourea (p. 394), and ethylene pseudo-thiourea (p. 396). It is produced by the action of brom-ethylamine hydrobromide (p. 163) upon potassium cyanate. It is a basic oil, which solidifies with difficulty (*Berichte*, 22, 1451).

Propylene-pseudo Urea, $C_3H_6{:}CON_2H_2$, is quite analogous. It results from HBr-propylamine and potassium cyanate, as well as from allyl urea, by a molecular rearrangement induced by hydrobromic acid (*Berichte*, 22, 2990).

2. DERIVATIVES OF UREA WITH ACID RADICALS, OR UREÏDES.

The derivatives of the monobasic acids are obtained in the action of acid chlorides or acid anhydrides upon urea. By this procedure, however, it is possible to introduce but one radical. The compounds are solids; they decompose when heat is applied to them, and do not form salts with acids. Alkalies cause them to separate into their components.

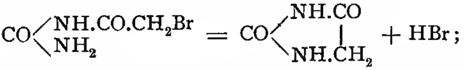
Acetyl Urea, $CO\!<\!\begin{smallmatrix} NH.C_2H_3O \\ NH_2 \end{smallmatrix}$, is not very soluble in cold water and alcohol. It forms long, silky needles, which melt at 112°. Heat breaks it up into acetamide and isocyanuric acid. *Chloracetyl urea*, $H_2N\ CO.NH.CO.CH_2Cl$, from urea and chloracetyl chloride, crystallizes in fine needles, which decompose about 160°. *Bromacetyl urea* dissolves with difficulty in water. When heated with ammonia it changes to hydantoïn (see above).

Methyl Acetyl Urea, $CO\!<\!\begin{smallmatrix} NH.C_2H_3O \\ NH.CH_3 \end{smallmatrix}$, is obtained from methyl urea upon digesting it with acetic anhydride, and by the action of bromine and potassium hydroxide upon acetamide (p. 160). It dissolves very readily in hot water, crystallizes in large prisms and melts at 180°.

Diacetyl Urea, $CO\!<\!\begin{smallmatrix} NH.C_2H_3O \\ NH.C_2H_3O \end{smallmatrix}$, results when $COCl_2$ acts on acetamide, $NH_2.C_2H_3O$, and sublimes in needles without decomposition.

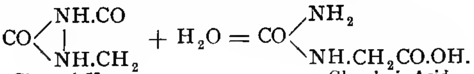
Derivatives of Urea with Divalent Acids :—

Glycolyl Urea, $C_3H_4N_2O_2$, **Hydantoïn,** is produced by heating bromacetyl urea with alcoholic ammonia :—



$$CO\!<\!\begin{matrix} NH.CO.CH_2Br \\ NH_2 \end{matrix} = CO\!<\!\begin{matrix} NH.CO \\ | \\ NH.CH_2 \end{matrix} + HBr;$$

and from allantoïn, and from alloxanic acid by heating with hydriodic acid. It crystallizes from hot water and alcohol, in needles, which melt at 216°, and show a neutral reaction. When boiled with baryta water, it passes into glycoluric acid :—

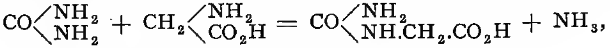


$$CO\!<\!\begin{matrix} NH.CO \\ | \\ NH.CH_2 \end{matrix} + H_2O = CO\!<\!\begin{matrix} NH_2 \\ \\ NH.CH_2CO.OH. \end{matrix}$$

Glycolyl Urea. Glycoluric Acid.

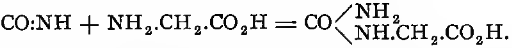
Nitrohydantoïn, $C_3H_3(NO_2)N_2O_2$, is produced when very strong nitric acid acts upon hydantoïn. It melts at 170°. The alkyl hydantoïns react in like manner (*Berichte*, 21, 2320; 22, Ref. 58).

Glycoluric Acid, $C_3H_6N_2O_3$, **Hydantoïc Acid**, was originally obtained from uric acid derivatives (allantoïn, glyco-uril, hydantoïn), but may be synthesized by heating urea with glycocoll, to 120°:—



$$CO\left\langle\begin{array}{l}NH_2\\NH_2\end{array}\right. + CH_2\left\langle\begin{array}{l}NH_2\\CO_2H\end{array}\right. = CO\left\langle\begin{array}{l}NH_2\\NH.CH_2.CO_2H\end{array}\right. + NH_3,$$

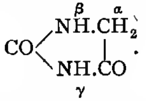
or by digesting glycocoll sulphate with potassium isocyanate:—



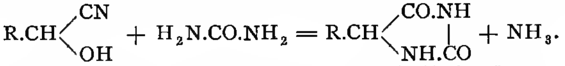
$$CO{:}NH + NH_2.CH_2.CO_2H = CO\left\langle\begin{array}{l}NH_2\\NH.CH_2.CO_2H.\end{array}\right.$$

Hydantoïc acid is very soluble in hot water and alcohol. It crystallizes in large, rhombic prisms. It is a monobasic acid, whose salts are generally very readily soluble; when heated with hydriodic acid they yield CO_2,NH_3 and glycocoll.

Hydantoïn contains a *closed* or *ring-shaped* nucleus of five members, consisting of three C-atoms and two nitrogen atoms. In this respect it resembles the glyoxalines or imido-azoles. The hydantoïn ring is, however, not very stable, owing to the presence of two CO-groups. The alkylic hydantoïns are derived by the replacement of the hydrogen atoms of the CH_2- and the two NH-groups. They are known as α-, β- and γ-derivatives, and are represented as follows:—



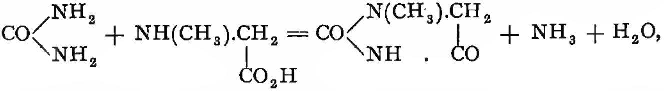
The α-derivatives may be synthesized by heating the cyanhydrins of the aldehydes and ketones (p. 203) with urea (see α-phenyl-hydantoïn, and *Berichte*, 21, 2320):—



$$R.CH\left\langle\begin{array}{l}CN\\OH\end{array}\right. + H_2N.CO.NH_2 = R.CH\left\langle\begin{array}{l}CO.NH\\NH.CO\end{array}\right. + NH_3.$$

α-Alkyt-hydantoïn.

β-**Methyl-hydantoïn**, $C_3H_3(CH_3)N_2O_2$, was first obtained from creatinine, and is also formed when sarcosine (p. 370) is heated with urea:—

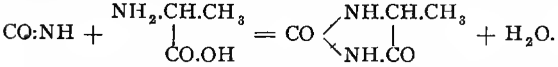


$$CO\left\langle\begin{array}{l}NH_2\\NH_2\end{array}\right. + \begin{array}{l}NH(CH_3).CH_2\\ \quad\quad\quad\quad\ \ CO_2H\end{array} = CO\left\langle\begin{array}{l}N(CH_3).CH_2\\NH\ .\ CO\end{array}\right. + NH_3 + H_2O,$$

or by heating the sarcosine with cyanogen chloride (*Berichte*, 15, 211). It forms soluble prisms which melt at 157°, and sublime in shining needles. It forms metallic derivatives on boiling with silver or mercury oxide, when the hydrogen of the imid-group suffers replacement.

β-**Ethyl-hydantoïn**, $C_3H_3(C_2H_5)N_2O_2$. It is formed like the preceding, and crystallizes in rhombic plates which melt at 100° and sublime readily.

α-**Lactyl Urea**, $C_4H_6N_2O_2$, α-**Methyl-hydantoïn**. It is formed from aldehyde ammonia along with alanine (p. 371), if cyanide of potassium, containing potassium isocyanate, be used in its preparation. It is very likely that then the alanine (α-amidopropionic acid) first produced acts upon the cyanic acid (as in the formation of hydantoïc acid) (*Berichte*, 21, 516):—

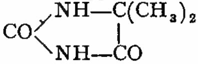


$$CO{:}NH + \begin{matrix}NH_2.CH.CH_3\\ |\\ CO.OH\end{matrix} = CO\left\langle\begin{matrix}NH.CH.CH_3\\ |\\ NH.CO\end{matrix}\right. + H_2O.$$

α-Amido-Propionic Acid. Lactyl Urea.

It has one molecule of H_2O, and crystallizes in large, rhombic prisms, which effloresce on exposure. It melts at 140–145°, and sublimes with partial decomposition. Boiled with baryta it absorbs water and forms *a-Lacturic Acid*, $CO\left\langle\begin{matrix}NH.CH(CH_3).CO_2H\\ NH_2\end{matrix}\right.$, which melts at 155°.

Acetonyl Urea, $C_5H_8N_2O_2$ =



$$CO\left\langle\begin{matrix}NH—C(CH_3)_2\\ \quad\quad |\\ NH—CO\end{matrix}\right.$$

, **α-Dimethyl-hydantoïn**, the ureïde of α-oxyisobutyric acid, $(CH_3)_2.C(HO).CO_2H$, is obtained like the preceding compound, on heating acetone and potassium cyanide (containing potassium isocyanate) with fuming hydrochloric acid. It is very soluble in water, and crystallizes in large prisms, which melt at 175° and sublime in needles. When heated to 160° with fuming hydrochloric acid, it breaks up into α-oxyisobutyric acid, NH_3 and CO_2. Boiling baryta water converts it into acetonyluric acid, $H_2N.CO.NH.C(CH_3)_2.CO_2H$, which fuses at 155–160°.

The ureïdes of the dibasic acids and those of glyoxylic acid, $CHO.CO_2H$, will receive attention under the uric acid derivatives. We will yet mention those of carbonic acid: allophanic acid, biuret and carbonyl diurea.

Allophanic Acid, $CO\left\langle\begin{matrix}NH_2\\ NH.CO_2H\end{matrix}\right.$, is not known in a free state. Its esters are formed when chlorcarbonic esters act upon urea:—

$$CO\left\langle\begin{matrix}NH_2\\ NH_2\end{matrix}\right. + CClO.O.C_2H_5 = CO\left\langle\begin{matrix}NH_2\\ NH.CO_2.C_2H_5\end{matrix}\right. + HCl;$$

or by leading cyanic acid vapors into the anhydrous alcohols: $2CO{:}NH + C_2H_5.OH = NH_2.CO.NH.CO_2.C_2H_5$. At first carbamic acid esters are produced (p. 383); these combine with a second molecule of cyanic acid and yield allophanic esters (*Berichte*, 22, 1572). The action of urea chloride upon alcohols (p. 376) proceeds in a similar manner. The first products are carbamic esters. These unite with a second molecule of the chloride and produce allophanic esters: $Cl.CO.NH_2 + H_2N{:}CO.C_2H_5 = H_2N.CO.NH.CO_2.C_2H_5$ (*Berichte*, 21, Ref. 293). The allophanic esters are crystalline, dissolve with difficulty in water, and, when heated, split up into alcohol, ammonia and cyanuric acid. The allophanates are obtained from them by means of the alkalies or baryta water. They show an alkaline reaction and are decomposed by carbonic acid. On attempting to free the acid by means of mineral acids, it at once breaks up into CO_2 and urea.

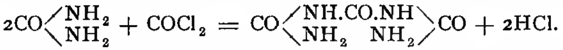
Ethyl Allophanic Ester, $NH_2.CO.NH.CO_2.C_2H_5$, is obtained when hydrochloric acid acts upon a solution of potassium isocyanate dissolved in alcohol. Shining needles, melting at 190–191°. The *propyl ester* melts at 155°.

Allophanamide, $CO\left\langle\begin{matrix}NH\\ NH.CO.NH_2\end{matrix}\right.$, **Biuret,** is formed on heating the allophanic esters with ammonia to 100°, or urea to 150–160°:—

$$2CO\left\langle\begin{matrix}NH_2\\ NH_2\end{matrix}\right. = CO\left\langle\begin{matrix}NH_2\\ NH.CO.NH_2\end{matrix}\right. + NH_3.$$

It is readily soluble in alcohol and water, and crystallizes with 1 molecule of water, in the form of warts and needles. When anhydrous, biuret melts at 190°, and decomposes further into NH_3 and cyanuric acid. The aqueous solution, containing KOH, is colored a violet red by copper sulphate. Heated in a current of HCl, biuret decomposes into NH_3, CO_2, cyanuric acid, urea and guanidine.

Carbonyl Diurea, $C_3H_6N_4O_3$, is formed on heating urea with $COCl_2$ to 100°:—



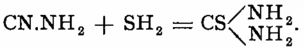
$$2CO\left\langle\begin{matrix}NH_2\\NH_2\end{matrix}\right. + COCl_2 = CO\left\langle\begin{matrix}NH.CO.NH\\NH_2 \quad NH_2\end{matrix}\right\rangle CO + 2HCl.$$

It is a crystalline powder, not readily dissolved by water. Heat converts it into ammonia and cyanuric acid.

Thio-urea, Sulphocarbamide, $CS\left\langle\begin{matrix}NH_2^{*}\\NH_2\end{matrix}\right.$. It is obtained by heating ammonium thiocyanate to 170°, when a transposition, analogous to that occurring in the formation of urea, takes place (p. 387):—

$$CS{:}N.NH_4 \text{ yields } CS\left\langle\begin{matrix}NH_2\\NH_2\end{matrix}\right.;$$

and by the action of hydrogen sulphide (in presence of a little ammonia), or ammonium thiocyanate upon cyanamide:—



$$CN.NH_2 + SH_2 = CS\left\langle\begin{matrix}NH_2\\NH_2\end{matrix}\right..$$

Preparation.—Heat dried ammonium thiocyanate to 180° for several hours. The mass is then treated with an equal weight of hot water and the filtered solution allowed to crystallize (*Annalen*, 179, 113).

Sulphocarbamide crystallizes in fine, silky needles, or in thick, rhombic prisms, which dissolve easily in water and alcohol, but with difficulty in ether; they possess a bitter taste and have a neutral reaction. They melt at 169° (*Berichte*, 18, 461) and decompose at higher temperatures. When sulphocarbamide is heated with water to 140° it again becomes ammonium thiocyanate. If boiled with alkalies, hydrochloric acid or sulphuric acid, it decomposes according to the equation:—

$$CSN_2H_4 + 2H_2O = CO_2 + 2NH_3 + H_2S.$$

Nitrous acid eliminates nitrogen. Silver, mercury, or lead oxide and water will convert it, at ordinary temperatures, into cyanamide, CN_2H_2; and on boiling into dicyandiamide (p. 289).

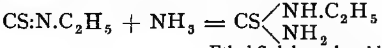
---

[*] The hypothetical isothio-urea or imido-thiocarbamic acid, $HN = C\left\langle\begin{matrix}NH_2\\SH\end{matrix}\right.$, is isomeric with thio urea. It is, however, only known in its derivatives (p. 396 and phenyl-isothiourea). Both are probably tautomeric and change into each other, while their alkyl derivatives are isomeric (p. 54, and *Berichte*, 18, 3103; 21, 1859).

Thio-urea combines with 1 equivalent of acid to form salts. The *nitrate*, $CSN_2H_4.HNO_3$, occurs in large crystals. Auric chloride and platinic chloride throw down red colored double chlorides from the concentrated solution. Silver nitrate precipitates $(CSN_2H_4)_2.Ag_2O + 4H_2O$, and mercuric nitrate, $(CSN_2H_4)_2$ $3HgO + 3H_2O$ (see *Berichte*, 17, 297).

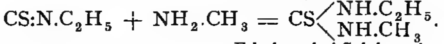
Compound Sulphocarbamides, in which hydrogen is replaced by alcohol radicals, are formed :—

(1) On heating the mustard oils (p. 279) with amine bases :—



$$CS{:}N.C_2H_5 + NH_3 = CS\begin{matrix}\diagup NH.C_2H_5\\ \diagdown NH_2\end{matrix}$$

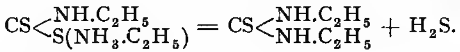
Ethyl Sulphocarbamide



$$CS{:}N.C_2H_5 + NH_2.CH_3 = CS\begin{matrix}\diagup NH.C_2H_5\\ \diagdown NH.CH_3\end{matrix}.$$

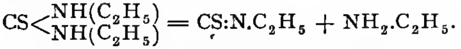
Ethyl-methyl Sulphocarbamide.

(2) By heating the amide salts of the alkyl dithiocarbamic acids (p. [illegible]85) :—



$$CS\begin{matrix}\diagup NH.C_2H_5\\ \diagdown S(NH_3.C_2H_5)\end{matrix} = CS\begin{matrix}\diagup NH.C_2H_5\\ \diagdown NH.C_2H_5\end{matrix} + H_2S.$$

The sulphocarbamides regenerate amines and mustard oils by distillation with P_2O_5, or when heated in HCl-gas :—



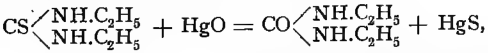
$$CS\begin{matrix}\diagup NH(C_2H_5)\\ \diagdown NH(C_2H_5)\end{matrix} = CS{:}N.C_2H_5 + NH_2.C_2H_5.$$

Ethyl Sulphocarbamide, $CS\begin{matrix}\diagup NH.C_2H_5\\ \diagdown NH_2\end{matrix}$, crystallizes in needles, melting at 106°.

Diethyl Sulphocarbamide, $CS\begin{matrix}\diagup NH.C_2H_5\\ \diagdown NH.C_2H_5\end{matrix}$, consists of large crystals, not very soluble in water. It melts at 77°.

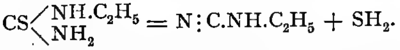
Methyl Ethyl Sulphocarbamide, $CS\begin{matrix}\diagup NH.CH_3\\ \diagdown NH.C_2H_5\end{matrix}$, is derived from ethyl mustard oil and methylamine. It melts at 54°.

The sulphur in the alkylic sulphocarbamides may be replaced by oxygen if these compounds are boiled with water and mercuric oxide. Those that contain two alkyl groups yield the corresponding ureas :—



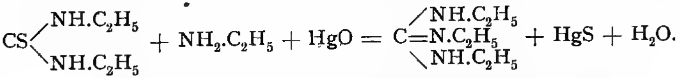
$$CS\begin{matrix}\diagup NH.C_2H_5\\ \diagdown NH.C_2H_5\end{matrix} + HgO = CO\begin{matrix}\diagup NH.C_2H_5\\ \diagdown NH.C_2H_5\end{matrix} + HgS,$$

whereas the mono-derivatives pass into alkylic cyanamides (and melamines) after parting with hydrogen sulphide (p. 289) :—



$$CS\begin{matrix}\diagup NH.C_2H_5\\ \diagdown NH_2\end{matrix} = N{:}C.NH.C_2H_5 + SH_2.$$

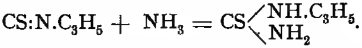
On digesting the dialkylic sulphocarbamides with mercuric oxide and amines, oxygen is exchanged for the imid-group and guanidine derivatives appear (p. 295) :—



$$CS\begin{matrix}\diagup NH.C_2H_5\\ \\ \diagdown NH.C_2H_5\end{matrix} + NH_2.C_2H_5 + HgO = C\begin{matrix}\diagup NH.C_2H_5\\ =N.C_2H_5\\ \diagdown NH.C_2H_5\end{matrix} + HgS + H_2O.$$

Consult *Berichte*, 23, 283, upon the different propyl-sulphocarbamides.

Allyl Sulphocarbamide, $CS{<}\begin{matrix}NH.C_3H_5\\NH_2\end{matrix}$, **Thio-sinamine**, is formed by the union of allyl mustard oil with ammonia:—

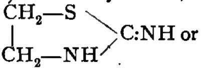


$$CS{:}N.C_3H_5 + NH_3 = CS{<}\begin{matrix}NH.C_3H_5\\NH_2\end{matrix}.$$

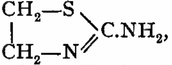
It forms shining prisms, with bitter taste, and melts at 74°. It decomposes at higher temperatures. It is readily soluble in water, alcohol and ether; combines with one equivalent of acid, and forms salts with acid reaction. Water decomposes them. Allyl cyanamide and triallyl-melamine are produced on boiling with mercuric oxide or lead hydroxide (p. 289). For the constitution of the dialkyl sulphocarbamides compare diphenyl-sulphocarbamides and *Berichte*, 23, 271.

Ethylene Sulphocarbamide, $CS{<}\begin{matrix}NH\\NH\end{matrix}{>}C_2H_4$, is obtained from ethylene-diamine and carbon disulphide (*Berichte*, 5, 242). It is crystalline, and melts at 194°. It does not combine with acids.

Ethylene-pseudo(iso) Sulphocarbamide,



or

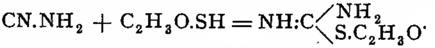


is isomeric with the preceding. It is a derivative of pseudo-sulphocarbamide (p. 391). It is obtained from HBr-ethyleneamine (p. 163) and potassium thiocyanate. Bromethyl-sulphocarbamide, $CH_2Br.CH_2.NH.CS.NH_2$, is formed at first and splits off hydrobromic acid. Ethylene pseudo-sulphocarbamide is a base with strong basic properties. Its salts crystallize well. Alkalies separate it from these in the form of an oil. This in time solidifies and then melts at 85° (*Berichte*, 22, 1141).

Propylene-pseudo-thio-urea, $C_3H_6{:}CSN_2H_2$, from brompropylamine and potassium thiocyanate, is perfectly similar. It also results from allyl thiourea by action of hydrobromic acid (*Berichte*, 22, 2984; 23, 964).

Acetyl sulphocarbamide and Thiohydantoïn are considered as *acid derivatives* of sulphocarbamide. The latter is undoubtedly a derivative of the isomeric iso-thiocarbamide (p. 394).

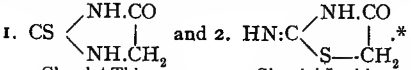
Acetyl Sulphocarbamide, $CS{<}\begin{matrix}NH_2\\NH.C_2H_3O\end{matrix}$, or $HN = C{<}\begin{matrix}NH_2\\S.C_2H_3O\end{matrix}$, is obtained from thio-urea by heating it with acetic anhydride. Its formation from cyanamide (carbodiimide, p. 288) and thio-acetic acid argues for the second formula:—



$$CN.NH_2 + C_2H_3O.SH = NH{:}C{<}\begin{matrix}NH_2\\S.C_2H_3O\end{matrix}.$$

It crystallizes from hot water in prisms; these melt at 165°.

The so-called **Thio- or Sulpho-hydantoïn**, $C_3H_4N_2SO$, is not constituted according to the formula 1, corresponding to that of hydantoïn (p. 391), but according to 2:—



Glycolyl Thio-urea. Glycolyl Isothio-urea.

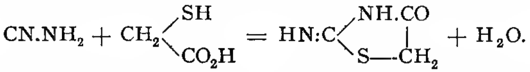
---

* Real sulphohydantoïns (of the formula 1) have been prepared in the benzene series (see phenyl sulphhydantoïn and *Berichte*, 17, 425).

The grouping (*Annalen*, 207, 121) in this instance is analogous to that shown by the isothio-amides (p. 260) and the phenyl isothiourethanes (p. 396).

The closed, *five-membered* ring in thiohydantoïn and in ethylene pseudo-thiourea consists of three C-atoms, one N-atom, and one S-atom. It is known as the *Thiazoline*-ring. It is closely allied to thiazole derivatives (see these).

Sulphohydantoïn is obtained when chloracetic acid and its anhydride act on sulphocarbamide; or (analogous to the formation of acetylsulphocarbamide) by evaporating an aqueous solution of cyanamide and thioglycollic acid (p. 355), when the sulphohydantoïc acid (see below), produced at first, parts with a molecule of water:—



$$CN.NH_2 + CH_2\begin{cases}SH\\CO_2H\end{cases} = HN:C\begin{cases}NH.CO\\ \quad\ \ |\\S\text{—}CH_2\end{cases} + H_2O.$$

Sulphohydantoïn crystallizes from hot water in long needles, and decomposes near 200°. When boiled with baryta water it decomposes into thioglycollic acid and dicyandiamide. Unlike the thio-ureas, it is not desulphurized when boiled with lead oxide or mercuric oxide and water.

Boiling acids convert it into *mustard-oil acetic acid*, with elimination of NH_3.

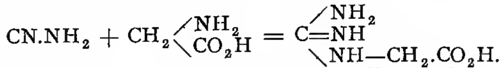
Isonitrosohydantoïn (*Berichte*, 19, Ref. 14) is produced by the action of nitrous acid upon it.

Sulphohydantoïc Acid, $C_3H_6N_2SO_2 = HN:C\begin{cases}NH_2\\S.CH_2.CO_2H,\end{cases}$ is obtained by heating sulphocarbamide with sodium chloracetic acid. It is a crystalline compound, not very soluble in water. It resembles the amido-acids in having a neutral reaction, but dissolves in alkalies and acids with production of salts. When heated with acids it reverts to thiohydantoïn.

GUANIDINE DERIVATIVES.

Guanidine, like urea, is capable of yielding acid derivatives (p. 296), but few of them, however, are known. Creatine and creatinine, compounds of great significance physiologically, belong in this class and are derived from glycocyamine.

Glycocyamine, $C_3H_7N_3O_2$, guanidoacetic acid, is obtained by the direct union of glycocoll with cyanamide:—



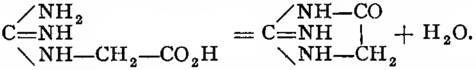
$$CN.NH_2 + CH_2\begin{cases}NH_2\\CO_2H\end{cases} = C\begin{cases}NH_2\\=NH\\NH\text{—}CH_2.CO_2H.\end{cases}$$

Cyanamide. Glycocoll. Glycocyamine.

On mixing the aqueous solutions it separates after a time in granular crystals. It is soluble in 120 parts cold water and rather readily in hot water; while it is insoluble in alcohol and ether. It forms crystalline compounds with acids and bases. When boiled with water and lead peroxide, or with dilute sulphuric acid, it breaks down into guanidine, oxalic acid and carbon dioxide.

β-Guanidopropionic Acid, $C_4H_9N_3O_2$ (alacreatine, $CN_3H_4.CH_2.CH_2.CO_2H$), is homologous with the preceding, and is obtained in a similar manner from cyanamide and β-amidopropionic acid. It decomposes at 205°. Isomeric α-guanidopropionic acid melts at 180°.

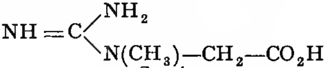
Glycocyamidine, $C_3H_5N_3O$, glycolyl guanidine, bears the same relation to glycocyamine as hydantoïn to hydantoïc acid (p. 391). Its hydrochloride is produced when glycocyamine hydrochloride is heated to 160°:—



$$C\begin{cases}NH_2\\=NH\\NH-CH_2-CO_2H\end{cases} = C\begin{cases}NH-CO\\=NH \quad |\\NH-CH_2\end{cases} + H_2O.$$

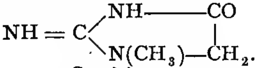
The free base crystallizes in deliquescent laminæ, having an alkaline reaction. $PtCl_4$ precipitates its hydrochloride.

The methyl derivatives of glycocyamine and glycocyamidine are:—



$$NH=C\begin{cases}NH_2\\N(CH_3)-CH_2-CO_2H\end{cases}$$

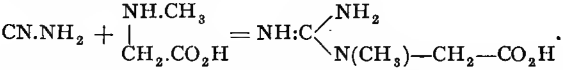
Creatine.



$$NH=C\begin{cases}NH-CO\\ \qquad\quad |\\N(CH_3)-CH_2.\end{cases}$$

Creatinine.

Creatine, $C_4H_9N_3O_2$, methyl glycocyamine, occurs in the animal organism, especially in the juice of muscles. It may be artificially prepared, like glycocyamine, by the union of sarcosine (methyl glycocoll) with cyanamide:—

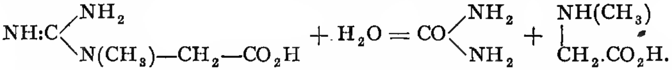


$$CN.NH_2 + \begin{array}{l}NH.CH_3\\|\\CH_2.CO_2H\end{array} = NH:C\begin{cases}NH_2\\N(CH_3)-CH_2-CO_2H\end{cases}.$$

To obtain creatine, exhaust finely divided flesh with cold water, boil the solution to coagulate the albumen, precipitate the phosphoric acid in the filtrate with baryta water and evaporate the liquid, then let it crystallize.

Creatine crystallizes with one molecule of water in glistening prisms. Heated to 100°, they sustain a loss of water. It reacts neutral, has a faintly bitter taste and dissolves rather readily in boiling water; it dissolves with difficulty in alcohol, and yields crystalline salts with one equivalent of acid.

When digested with acids, creatine loses water and becomes creatinine (see above), and with baryta water it falls into urea and sarcosine:—

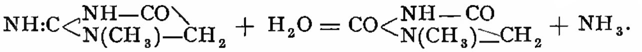


$$NH:C\begin{cases}NH_2\\N(CH_3)-CH_2-CO_2H\end{cases} + H_2O = CO\begin{cases}NH_2\\NH_2\end{cases} + \begin{array}{l}NH(CH_3)\\|\\CH_2.CO_2H.\end{array}$$

Ammonia is liberated at the same time and methyl hydantoïn (p. 392) is formed. When its aqueous solution is heated with mercuric oxide, creatine becomes oxalic acid and methyl guanidine. Ammonia and methylamine are disengaged when it is ignited with soda lime.

Creatinine, $C_4H_7N_3O$, methyl glycocyamidine, occurs constantly in urine (about 0.25 per cent.), and is readily obtained from creatine by evaporating its aqueous solution, especially when acids are present. It crystallizes in rhombic prisms and is much more soluble than creatine, in water and alcohol. It is a strong base which can expel ammonia from ammonium salts and yields well crystallized salts with acids. Its compound with zinc chloride, $(C_4H_7N_3O)_2.ZnCl_2$, is particularly characteristic. Zinc chloride precipitates it from creatinine solutions as a crystalline powder, dissolving with difficulty in water.

Bases cause creatinine to absorb water and become creatine again. Boiled with baryta water it decomposes into methyl hydantoïn and ammonia :—



$$NH{:}C\!<\!\begin{matrix}NH-CO\diagdown\\N(CH_3)-CH_2\end{matrix} + H_2O = CO\!<\!\begin{matrix}NH-CO\\N(CH_3)-CH_2\end{matrix} + NH_3.$$

When boiled with mercuric oxide it breaks up like creatine into methyl-guanidine and oxalic acid.

When creatinine is heated with alcoholic ethyl iodide, the ammonium iodide of ethyl creatinine, $C_4H_7(C_2H_5)N_3O.I$, is produced. Silver oxide converts this into the ammonium base, $C_4H_7(C_2H_5)N_3O.OH$.

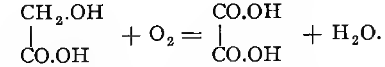
DIBASIC ACIDS, $C_nH_{2n-2}O_4$.

Oxalic	Acid	$C_2H_2O_4$	$= (CO_2H)_2$
Malonic	"	$C_3H_4O_4$	$= CH_2(CO_2H)_2$
Succinic	Acids	$C_4H_6O_4$	$= C_2H_4(CO_2H)_2$
Pyrotartaric	Acid	$C_5H_8O_4$	$= C_3H_6(CO_2H)_2$
Adipic	"	$C_6H_{10}O_4$	$= C_4H_8(CO_2H)_2$, etc.

The acids of this series contain two carboxyl groups, hence are *dibasic*. They are produced according to methods analogous to those employed with the monobasic acids, by a repetition of the formation of the carboxyl group.

The most important general methods are :—

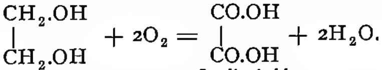
(1) By oxidation of oxy-fatty acids, in which OH is linked to CH_2 :—



$$\begin{matrix}CH_2.OH\\|\\CO.OH\end{matrix} + O_2 = \begin{matrix}CO.OH\\|\\CO.OH\end{matrix} + H_2O.$$

Glycollic Acid. Oxalic Acid.

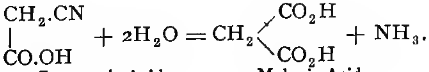
(2) By oxidation of the corresponding dihydric alcohols :—



$$\begin{matrix}CH_2.OH\\|\\CH_2.OH\end{matrix} + 2O_2 = \begin{matrix}CO.OH\\|\\CO.OH\end{matrix} + 2H_2O.$$

Oxalic Acid.

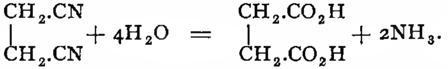
(3) Conversion of monohalogen substituted fatty-acids into cyan-derivatives, and boiling the latter with alkalies or acids (pp. 211 and 282) :—



$$\begin{matrix}CH_2.CN\\|\\CO.OH\end{matrix} + 2H_2O = CH_2\!<\!\begin{matrix}CO_2H\\CO_2H\end{matrix} + NH_3.$$

Cyanacetic Acid. Malonic Acid.

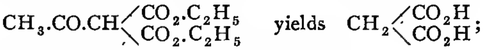
(4) Conversion of the halogen addition products of the alkylens, C_nH_{2n}, into cyanides and the saponification of the latter:—



$$\begin{array}{l}CH_2.CN\\ |\\ CH_2.CN\end{array} + 4H_2O = \begin{array}{l}CH_2.CO_2H\\ |\\ CH_2.CO_2H\end{array} + 2NH_3.$$

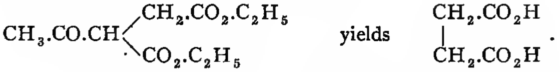
Only the halogen products having their halogen atoms attached to two different carbon atoms can be converted into dicyanides.

(5) A very general method for the synthesis of dibasic acids is founded upon the transposition of aceto-acetic esters. Acid residues are introduced into the latter and the products decomposed by concentrated alkali solutions (p. 341). Thus from aceto-malonic ester we get malonic acid.—



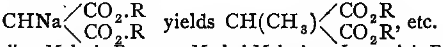
$$CH_3.CO.CH\langle\begin{array}{l}CO_2.C_2H_5\\ CO_2.C_2H_5\end{array} \text{ yields } CH_2\langle\begin{array}{l}CO_2H\\ CO_2H\end{array};$$

and from aceto-succinic ester, succinic acid:—



$$CH_3.CO.CH\langle\begin{array}{l}CH_2.CO_2.C_2H_5\\ \\ CO_2.C_2H_5\end{array} \text{ yields } \begin{array}{l}CH_2.CO_2H\\ |\\ CH_2.CO_2H\end{array}.$$

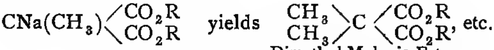
(6) In a perfectly similar manner, higher dibasic acids can be prepared from malonic esters, $CH_2(CO_2R)_2$. One hydrogen atom of CH_2 is replaced by sodium and then the alkyls introduced by means of the alkyl iodides:—



$$CHNa\langle\begin{array}{l}CO_2.R\\ CO_2.R\end{array} \text{ yields } CH(CH_3)\langle\begin{array}{l}CO_2R\\ CO_2R'\end{array}, \text{ etc.}$$

Sodium Malonic Ester. Methyl Malonic or Isosuccinic Ester.

In these monoalkylic esters the second hydrogen atom can be replaced by sodium and alkyls:—



$$CNa(CH_3)\langle\begin{array}{l}CO_2R\\ CO_2R\end{array} \text{ yields } \begin{array}{l}CH_3\\ CH_3\end{array}\rangle C\langle\begin{array}{l}CO_2R\\ CO_2R'\end{array}, \text{ etc.}$$

Dimethyl Malonic Ester.

The free acids are obtained by saponifying the esters with alkalies.

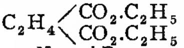
In performing these syntheses the malonic ester is mixed with the theoretical amount of sodium dissolved in absolute alcohol (10 volumes), the alkyl iodide added, and heat applied until the alkaline reaction disappears. After expelling the excess of alcohol, the ester is precipitated with water (in preparing the dialkyl derivatives 2 equivalents of sodium alcoholate and alkyl iodide are added. *Annalen*, 204, 129). Tri- and poly-carboxylic acids may likewise be obtained by the introduction of acid esters (by means of chloracetic ester, etc. (p. 341 and *Berichte*, 15, 1109). The synthesis of the alkyl derivatives may also be effected by means of the alkyl iodides and zinc (*Berichte*, 20, 203). Allyl iodide reacts similarly with zinc (*Berichte*, 21, Ref. 181).

The dibasic acids are also formed on oxidizing the fatty acids $C_nH_{2n}O_2$, the acids of the oleic acid series, and the fats with nitric acid. Potassium permanganate oxidizes some hydrocarbons, C_nH_{2n}, to dibasic acids.

The acids of this series are solids, crystallizable, and generally volatile without decomposition. They are mostly soluble in water and have a strong acid reaction. The melting points of the normal dicarboxylic acids exhibit the same regularity observed with the fatty acids (p. 215), *i. e.*, the members containing an even number of carbon atoms melt higher than those with an odd number (*Berichte*, 10, 1286). The melting points of both series fall with increasing carbon content (*Berichte*, 18, Ref. 59).

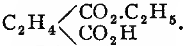
At higher temperatures those members which are capable of yielding anhydrides part with water and pass into such compounds, whereas, the others, *having both carboxyl groups attached to one carbon atom*, decompose more or less readily into CO_2 and monobasic fatty-acids (p. 211). Thus, from oxalic acid we get formic acid, from malonic acid, $CH_2(CO_2H)_2$, acetic acid, from isosuccinic acid, $CH_3.CH(CO_2H)_2$, propionic acid, etc. Similarly, malonic acid, and mono-alkyl malonic acids, $R.CH(CO_2H)_2$, are decomposed, at the ordinary temperature, by concentrated nitric acid, with the evolution of two molecules of carbon dioxide, while the dialkyl malonic acids, $R_2C(CO_2H)_2$, and succinic, pyrotartaric and the unsaturated acids, fumaric and maleïc, etc., are unattacked by cold nitric acid (*Berichte*, 18, Ref. 146; 19, Ref. 337).

Having two carboxyls, the dibasic acids can form neutral and acid salts, likewise neutral and acid esters or ether-acids (similar to sulphuric acid) :—



$$C_2H_4\begin{cases}CO_2.C_2H_5\\CO_2.C_2H_5\end{cases}$$

Neutral Ester.



$$C_2H_4\begin{cases}CO_2.C_2H_5.\\CO_2H\end{cases}$$

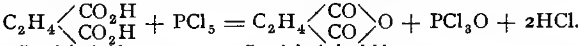
Primary Ester.

The best method to use in making the *neutral esters* is to dissolve the acid in alcohol, and while applying heat lead in a stream of hydrogen chloride gas; on adding water the ester is precipitated, and may then be purified either by distillation or crystallization.

See *Berichte*, 14, 2630, for the ester formation of dibasic acids (p. 251).

With the dibasic acids the *anhydride formation* takes place within *one* molecule and leads to the formation of *inner* anhydrides; those resulting from the union of two molecules are not known (p.

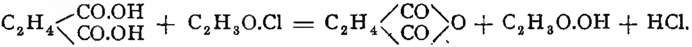
351). The anhydrides are obtained by either heating the acids (see above), or by the action of PCl_5 (1 molecule):—



$$C_2H_4\left<\begin{matrix}CO_2H\\CO_2H\end{matrix}\right. + PCl_5 = C_2H_4\left<\begin{matrix}CO\\CO\end{matrix}\right>O + PCl_3O + 2HCl.$$

Succinic Acid. Succinic Anhydride.

In many cases the analogous action of chlorides of the fatty acids, *e.g.*, acetyl chloride, on the free acids or their silver salts, is better adapted to the preparation of anhydrides (*Berichte*, 13, 1844):—



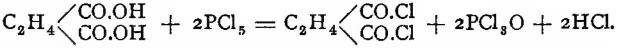
$$C_2H_4\left<\begin{matrix}CO.OH\\CO.OH\end{matrix}\right. + C_2H_3O.Cl = C_2H_4\left<\begin{matrix}CO\\CO\end{matrix}\right>O + C_2H_3O.OH + HCl.$$

It is a singular fact that anhydrides cannot be prepared from oxalic acid, $C_2O_4H_2$, malonic acid, $CH_2(CO_2H)_2$, isosuccinic acid, $CH_3.CH(CO_2H)_2$, etc., whereas succinic acid, normal pyrotartaric acid, also maleïc and phthalic acids are capable of such formations. It seems, then, that anhydrides are only possible with dicarboxylic acids (p. 352) in which there is a chain of four or five carbon atoms.*

The members obtained from succinic acid, by the entrance of alkylens, are more inclined to the formation of anhydrides according to the number of methyl groups they may contain (*Berichte*, 23, 101 and 620).

The anhydrides of this series are perfectly analogous in properties and transpositions to those of the fatty acids; they slowly dissolve in water, more readily on heating, with regeneration of their acids.

When two molecules of phosphorus pentachloride are permitted to act on the dicarboxylic acids chloranhydrides of the acids are formed:—

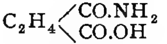


$$C_2H_4\left<\begin{matrix}CO.OH\\CO.OH\end{matrix}\right. + 2PCl_5 = C_2H_4\left<\begin{matrix}CO.Cl\\CO.Cl\end{matrix}\right. + 2PCl_3O + 2HCl.$$

These behave in all respects like monovalent acid chlorides.

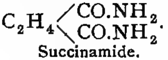
The divalent residues joined to the two OH's are termed the *radicals* of the dicarboxylic acids, *e. g.*, C_2O_2, oxalyl, $CH_2(CO)_2$, malonyl, $C_2H_4(CO)_2$, succinyl.

The *amides* are similar to those of the monobasic acids (p. 255). Both *acia amides* or *amic acids*, and the real *diamides* exist:—



$$C_2H_4\left<\begin{matrix}CO.NH_2\\CO.OH\end{matrix}\right.$$

Succinamic Acid.



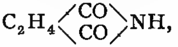
$$C_2H_4\left<\begin{matrix}CO.NH_2\\CO.NH_2\end{matrix}\right..$$

Succinamide.

---

* Malonic acid, succinic acid, and others, can be distilled without decomposition under reduced pressure. Adipic acid, $C_6H_{10}O_4$, is the first member of the series that can be distilled at the ordinary pressure without sustaining decomposition (*Berichte*, 22, 816).

The *imides* are derived by substituting divalent acid radicals for two hydrogen atoms in one molecule of ammonia (*Annalen*, 215, 172):—



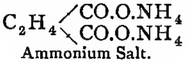
$$C_2H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle NH,$$

Succinimide.

The amide compounds may also be derived from the primary and neutral ammonium salts by the withdrawal of water:—

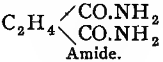
Acid Ammonium Salt — H_2O yields Amic Acid.
" " " — $2H_2O$ " Imide.
Neutral " " — $2H_2O$ " Amide.

By withdrawing 4 molecules of H_2O from the neutral salt the acid nitriles or cyanides of the divalent alcoholic radicals result (p. 265):—



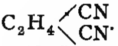
$$C_2H_4\left\langle\begin{matrix}CO.O.NH_4\\CO.O.NH_4\end{matrix}\right.$$

Ammonium Salt.



$$C_2H_4\left\langle\begin{matrix}CO.NH_2\\CO.NH_2\end{matrix}\right.$$

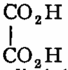
Amide.



$$C_2H_4\left\langle\begin{matrix}CN\\CN\end{matrix}\right. .$$

Nitrile.

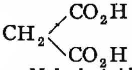
The possible cases of isomerism correspond with those of the C_nH_{2n} hydrocarbon groups; the two COOH groups may be attached to two different carbon atoms or to a single carbon atom. Isomerides of the first two members of the series—



$$\begin{matrix}CO_2H\\|\\CO_2H\end{matrix}$$

Oxalic Acid.

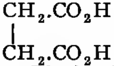
and



$$CH_2\left\langle\begin{matrix}CO_2H\\CO_2H\end{matrix}\right.$$

Malonic Acid.

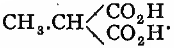
are not possible. For the third member two structural cases exist:—



$$\begin{matrix}CH_2.CO_2H\\|\\CH_2.CO_2H\end{matrix}$$

Ethylene Dicarboxylic Acid,
Succinic Acid.

and



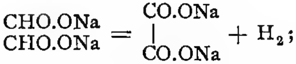
$$CH_3.CH\left\langle\begin{matrix}CO_2H\\CO_2H\end{matrix}\right. .$$

Ethidene Dicarboxylic Acid,
Isosuccinic Acid.

There are four possible isomerides with the formula $C_3H_6\left\langle\begin{matrix}CO_2H\\CO_2H\end{matrix}\right.$, etc. Many acids are named from malonic acid; this accords with their synthesis and is quite practicable (p. 400).

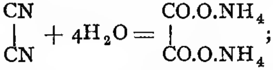
1. **Oxalic Acid**, $C_2O_4H_2$ (*Acidum oxalicum*), occurs in many plants, chiefly as potassium salt in the different varieties of *Oxalis* and *Rumex*. The calcium salt is often found crystallized in plant cells; it constitutes the chief ingredient of certain calculi. The acid may be prepared artificially by oxidizing many carbon compounds with nitric acid, or by fusing them with alkalies. It is

formed synthetically by rapidly heating sodium formate above 440°:—



$$\begin{array}{l}CHO.ONa\\CHO.ONa\end{array} = \begin{array}{l}CO.ONa\\|\\CO.ONa\end{array} + H_2;$$

by oxidizing formic acid with nitric acid (*Berichte*, 17, 9); by adding water to cyanogen:—



$$\begin{array}{l}CN\\|\\CN\end{array} + 4H_2O = \begin{array}{l}CO.O.NH_4\\|\\CO.O.NH_4\end{array};$$

and by conducting carbon dioxide over metallic sodium heated to 350–360°:—

$$2CO_2 + Na_2 = C_2O_4Na_2.$$

Formerly, the acid was obtained from the different oxalis species or by oxidizing sugar with nitric acid. At present it is prepared on an immense scale by fusing sawdust (cellulose) with a mixture of KOH and NaOH (equal parts) in iron pans and maintaining a temperature of 200–220°. The brown fusion is extracted with water and boiled with milk of lime. The separated calcium salt is decomposed with sulphuric acid and the filtrate evaporated to crystallization.

The ease with which sodium oxalate is produced from sodium formate (above), and the latter from CO and NaOH (p. 217) would make it appear possible to obtain the acid on a commercial scale by these reactions (*Berichte*, 15, 1508).

Oxalic acid with the formula, $C_2H_2O_4 + 2H_2O = C_2(OH)_6$, crystallizes in fine, transparent, monoclinic prisms, which effloresce at 20° in dry air and fall to a white powder. It is soluble in 9 parts of water of medium temperature, and quite easily in alcohol. The hydrated acid melts at 101° if rapidly heated, and the anhydrous at 189° (*Berichte*, 21, 1901). When carefully heated to 150° the anhydrous acid sublimes undecomposed; rapidly heated it decomposes into formic acid and carbon dioxide:—

$$C_2H_2O_4 = CH_2O_2 + CO_2.$$

Oxalic acid decomposes into carbonate and hydrogen by fusion with alkalies or soda-lime (p. 218):—

$$C_2O_4K_2 + 2KOH = 2CO_3K_2 + H_2.$$

Heated with concentrated sulphuric acid it yields carbon monoxide, dioxide and water:—

$$C_2H_2O_4 = CO_2 + CO + H_2O.$$

Nascent hydrogen (Zn and H_2SO_4) converts it into glycollic acid.

The oxalates, excepting those with the alkali metals, are almost insoluble in water.

The *neutral potassium salt*, $C_2O_4K_2 + H_2O$, is very soluble in water, and parts with its water of crystallization at 180°. The *acid salt*, C_2O_4HK, dissolves with more difficulty, and occurs in the juices of plants (of *Oxalis* and *Rumex*). *Potassium quadroxalate*, $C_2O_4KH, C_2O_4H_2 + 2H_2O$, forms triclinic crystals, soluble in 20 parts of water at 20°. Commercial salt of sorrel consists generally of a mixture of the acid and the super-salt.

Neutral Ammonium Oxalate $C_2O_4(NH_4)_2 + H_2O$, consists of shining, rhombic prisms, and is easily soluble in water. When heated it becomes oxamide, which further decomposes into C_2N_2, CO_2, CO and NH_3. *Acid ammonium oxalate*, $C_2O_4H(NH_4)$, yields oxamic acid on heating. The *calcium oxalate*, $C_2O_4Ca + H_2O$, is formed in a crystalline state in plant cells; it is precipitated as a white crystalline powder (quadratic octahedra) on the addition of an oxalate to a warm solution of a calcium salt. (A salt with $3H_2O$ separates from very dilute and cold solutions.) Calcium oxalate is insoluble in water and acetic acid, but is dissolved by the mineral acids. It parts with its water of crystallization at 200°. The *silver salt*, $C_2O_4Ag_2$, explodes when quickly heated.

ESTERS OF OXALIC ACID.

Oxalic Methyl Ester, $C_2O_2(O.CH_3)_2$, is obtained by distilling oxalic acid (1 part) or potassium oxalate (2 parts) with methyl alcohol (1 part) and sulphuric acid (1 part); or by boiling anhydrous oxalic acid with methyl alcohol. It forms large, rhombic plates, which are easily soluble in water and alcohol; possesses an aromatic odor, melts at 51° and distils at 163°. Water, especially when boiling, decomposes it into oxalic acid and methyl alcohol.

The *acid ester* (methyl oxalic acid), $\begin{array}{l} CO.O.CH_3 \\ | \\ CO.OH \end{array}$, is very unstable, and is found in the mother-liquor from the neutral ester.

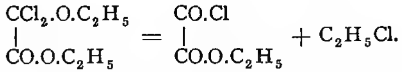
Oxalic Ethyl Ester, $C_2O_2(O.C_2H_5)_2$, is an aromatic-smelling liquid, of sp. gr. 1.0793 at 20° and boils at 186°. It dissolves with difficulty in water, and is gradually decomposed by it into oxalic acid and ethyl alcohol. It is produced by distilling equal parts of salt of sorrel, alcohol and sulphuric acid. The following method yields it more readily. Anhydrous oxalic acid (3 parts) is dissolved on the water bath, in absolute alcohol (2 parts), and the solution then introduced into a tubulated retort and heated to 100°. Gradually raising the temperature to 130°, the vapor of 2 parts absolute alcohol is conducted into the liquid; water and alcohol distil off. The oxalic ester is separated from the residue by fractional distillation (*Berichte*, 18, Ref. 221).

It forms oxamide and alcohol when shaken with aqueous ammonia; dry ammonia converts it into oxamic ester. *Potassium ethyl oxalate*, $C_2O_2\left\langle\begin{array}{l} O.C_2H_5 \\ OK, \end{array}\right.$ mixed with $C_2O_4K_2$, is precipitated by adding alcoholic potash to a solution of oxalic ester. The same salt is formed when monochloracetic ester is heated with KNO_2. It is a crystalline powder, which decomposes above 140°. Free *ethyl oxalic acid* is obtained by heating anhydrous oxalic acid with absolute alcohol, and distils undecomposed at 117° under 15 mm. pressure. Distilled under ordinary atmospheric pressure it decomposes into CO_2, formic ester and oxalic ester. See *Berichte*, 19, 1442; 22, 1807, for homologous alkyloxalic acids.

$POCl_3$ converts potassium ethyl oxalate into chloroxalic ester, $C_2O_2\left\langle\begin{array}{l} Cl \\ O.C_2H_5. \end{array}\right.$ A better method is to heat oxalic ester with PCl_5 until no more ethyl chloride is disengaged:—

$$\begin{array}{l} CO.O.C_2H_5 \\ | \\ CO.O.C_2H_5 \end{array} + PCl_5 = \begin{array}{l} CO.Cl \\ | \\ CO.O.C_2H_5 \end{array} + POCl_3 + C_2H_5Cl.$$

The first product is di-ethyl dichlorglycollic ester, which, upon distillation, separates into C_2H_5Cl and chloroxalic ester :—



$$\begin{array}{l} CCl_2.O.C_2H_5 \\ | \\ CO.O.C_2H_5 \end{array} = \begin{array}{l} CO.Cl \\ | \\ CO.O.C_2H_5 \end{array} + C_2H_5Cl.$$

This course is very convenient for the preparation of the ester of chloroxalic acid (*Berichte*, 19, 2159). The action of PCl_5 upon the homologues of oxalic ester is similar (*Berichte*, 19, 1443, Ref. 806).

When separated from the $POCl_3$ by fractional distillation, ethyl oxalyl chloride is a pungent-smelling liquid, boiling at 131.5°. It fumes strongly in the air and rapidly decomposes into oxalic acid. It sinks in water and gradually passes into oxalic acid, hydrochloric acid and alcohol. It reacts very energetically with alcohols and forms neutral esters. By further heating with PCl_5, it is slowly changed to trichloracetic ester.

The **Isoamyl Ester**, $C_2O_2(O.C_5H_{11})_2$, is obtained by heating amyl alcohol with oxalic acid. It is a thick oil which boils at 262°, and smells like bedbugs. Phosphorus pentachloride converts it into *amyl oxalyl chloride*, $C_2O_2\genfrac{}{}{0pt}{}{\diagup Cl}{\diagdown O.C_5H_{11}}$, an oil which partly decomposes on the application of heat (*Berichte*, 14, 1750); diamyl dichlorglycollic ester (*Berichte*, 19, 1443) is an intermediate product.

The **Allyl Ester**, $C_2O_2(O.C_3H_5)_2$, obtained by the action of allyl iodide on silver oxalate, boils at 206–207°, and has a specific gravity of 1.055.

AMIDES OF OXALIC ACID.

Oxamide, $C_2O_2(NH_2)_2$, separates as a white, crystalline powder, when neutral oxalic ester is shaken with aqueous ammonia. It is insoluble in water and alcohol. It is also formed when water and a trace of aldehyde act on cyanogen, C_2N_2, or by the direct union of hydrocyanic acid and hydrogen peroxide ($2CNH + H_2O_2 = C_2O_2N_2H_4$). Oxamide is partially sublimed when heated, the greater part, however, being decomposed. When heated to 200° with water, it is converted into ammonium oxalate.

Hydrorubianic Acid (p. 265) may be considered as **Dithio-oxamide**, $C_2S_2(NH_2)_2$, or isothio-oxamide, $C_2(SH)_2(NH_2)_2$.

The substituted oxamides containing alcohol radicals are produced by the action of the primary amines upon the oxalyl esters, *e.g.* :—

$C_2O_2\genfrac{}{}{0pt}{}{\diagup NH.CH_3}{\diagdown NH.CH_3}$

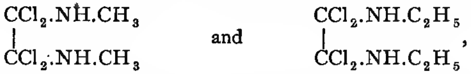
Dimethyl Oxamide.

$C_2O_2\genfrac{}{}{0pt}{}{\diagup NH.C_2H_5}{\diagdown NH.C_2H_5}$.

Diethyl Oxamide.

These compounds are more soluble in hot water and alcohol than oxamide, and distil without decomposition. The first melts at 210°. The alkalies break them up into oxalic acid and amines.

When two molecules of PCl_5 act upon dimethyl or diethyl oxamide the oxygen atoms are replaced by chlorine. The resulting amid-chlorides (p. 258) —

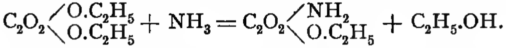


$$\begin{matrix}CCl_2.NH.CH_3\\ |\\ CCl_2.NH.CH_3\end{matrix} \quad\text{and}\quad \begin{matrix}CCl_2.NH.C_2H_5\\ |\\ CCl_2.NH.C_2H_5\end{matrix},$$

readily part with three molecules of HCl and yield chlorinated bases: *chloroxalmethylin*, $C_4H_5ClN_2$, and *chloroxalethylin*, $C_5H_9ClN_2$. Both are very alkaline liquids, soluble in water; the first boils at 205°, the second at 217–218°. On heating them with hydriodic acid and amorphous phosphorus we get bases that do not contain chlorine; **Oxalmethylin**, $C_4H_6N_2$, and **Oxalethylin**, $C_6H_{10}N_2$; the first is identical with methyl glyoxaline, the second with ethyl glyoxalethylin (p. 325).

Oxamic Acid, $C_2O_2\left\langle\begin{matrix}NH_2\\OH\end{matrix}\right.$, is obtained from its ammonium salt, which is produced by heating acid ammonium oxalate, or by boiling oxamide with ammonia, and then liberating the acid with hydrochloric acid (*Berichte*, 19, 3229). It is most easily obtained by boiling oxamethane with ammonia (*Berichte*, 22, 1569). It is a crystalline powder, that dissolves with difficulty in cold water, and melts at 173°. It is monobasic and forms crystalline salts. It passes into acid ammonium oxalate when heated with water.

Its *esters* result from the action of alcoholic, or dry ammonia upon the esters of oxalic acid:—



$$C_2O_2\left\langle\begin{matrix}O.C_2H_5\\O.C_2H_5\end{matrix}\right. + NH_3 = C_2O_2\left\langle\begin{matrix}NH_2\\O.C_2H_5\end{matrix}\right. + C_2H_5.OH.$$

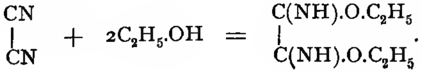
Ethyl Oxamic Ester (Oxamethane), $C_2O_2\left\langle\begin{matrix}NH_2\\O.C_2H_5\end{matrix}\right.$, consists of shining, fatty-feeling leaflets. It melts at 114–115° and boils at 200°. PCl_5 converts it into the *amid-chloride*, $CCl_2(NH_2).CO.O.C_2H_5$ (see above), a crystalline compound, which reverts to oxamethane, when exposed to moist air. HCl separates when heat is applied and the product is cyancarbonic ester, $CN.CO.O.C_2H_5$. Isomeric bodies, *alkylic oxamic acids*, are obtained by heating salts of the primary amines of oxalic acid. Ethyloxamic acid, $C_2O_2\left\langle\begin{matrix}NH.C_2H_5\\OH\end{matrix}\right.$, crystallizes in six-sided plates and melts at 120°.

Ethyl Dietho-oxamic Ester, $C_2O_2\left\langle\begin{matrix}N(C_2H_5)_2\\O.C_2H_5\end{matrix}\right.$ (Diethyloxamethane), boils at 254° and is produced by the action of diethylamine upon oxalic esters. It regenerates diethylamine on distilling with potash. A method for separating the amines (p. 158) is based on this behavior.

Oxalimide, $\left.\begin{matrix}CO\\ |\\ CO\end{matrix}\right\rangle NH$, is obtained from oxamic acid by the aid of PCl_5 or PCl_3O. It dissolves with difficulty in cold water, and crystallizes in shining needles from hot water. Boiling water decomposes it into oxalic acid and oxamide. Aqueous ammonia converts it into oxamide (*Berichte*, 19, 3229).

Cyanogen is the nitrile of oxalic acid (p. 263).

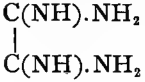
The *oximido-ether* is produced when HCl acts upon cyanogen in alcoholic solution:—



$$\begin{matrix}CN\\ |\\ CN\end{matrix} + 2C_2H_5.OH = \begin{matrix}C(NH).O.C_2H_5\\ |\\ C(NH).O.C_2H_5\end{matrix}.$$

This is analogous to the formation of the imido-ethers (p. 292) from nitriles.

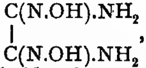
Alcoholic ammonia converts the product into *oxamidine*,



$$\begin{array}{l} C(NH).NH_2 \\ | \\ C(NH).NH_2 \end{array}$$

(*Berichte*, **16**, 1655).

Oxaldiamid-oxime,

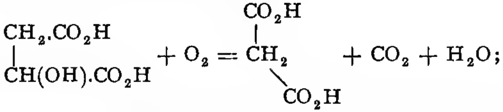


$$\begin{array}{l} C(N.OH).NH_2 \\ | \\ C(N.OH).NH_2 \end{array}$$

, the dioxime of oxamide, is formed when ammonia acts upon oximido-ether, or hydroxylamine (2 molecules) upon cyanogen, CN.CN, upon cyan-aniline, or hydrorubianic acid (p. 265). It crystallizes, from alcohol, in white needles, melting at 196°. It exhibits all the properties of the amidines, and dissolves in acids and alkalies (*Berichte*, **22**, 2942 and 2946).

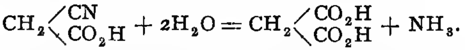
---

(2) **Malonic Acid**, $C_3H_4O_4 = CH_2(COOH)_2$, occurs in the deposit found in the vacuum pans employed in the beet sugar manufacture. It is obtained by the oxidation of malic acid (and hydracrylic acid) with chromic acid:—



$$\begin{array}{l} CH_2.CO_2H \\ | \\ CH(OH).CO_2H \end{array} + O_2 = \begin{array}{l} CO_2H \\ | \\ CH_2 \\ \diagdown \\ CO_2H \end{array} + CO_2 + H_2O;$$

by the decomposition of malonyl urea (barbituric acid, see this) with alkalies, and by the oxidation of propylene and allylene with potassium permanganate. It may be prepared, too, by boiling cyanacetic acid (p. 262) with alkalies or acids:—



$$CH_2\begin{array}{l} \diagup CN \\ \diagdown CO_2H \end{array} + 2H_2O = CH_2\begin{array}{l} \diagup CO_2H \\ \diagdown CO_2H \end{array} + NH_3.$$

Preparation.—100 grams of chloracetic acid, dissolved in 200 grams of water, are neutralized with sodium carbonate (110 grams), and to this 75 grams of pure, pulverized potassium cyanide are added, and the whole carefully heated, after solution, upon a water-bath. The cyanide produced is saponified either by concentrated hydrochloric acid or potassium hydroxide (*Berichte*, 13, 1358, and *Annalen*, 204, 125). To obtain the malonic ester directly, evaporate the cyanide solution, cover the residue with absolute alcohol and lead HCl gas into it (*Annalen*, 218, 131).

Malonic acid crystallizes in large tables or laminæ. It is easily soluble in water, alcohol and ether, and melts at 132°. At higher temperatures it decomposes into acetic acid and carbon dioxide. The ethyl ester is similarly broken up into CO_2 and acetic ester when it is heated with water to 150° Bromine in aqueous solution converts it into tribromacetic acid and CO_2. Its *barium salt*,

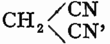
$(C_3H_2O_4)Ba + 2H_2O$, forms silky, shining needles. The *calcium salt*, $(C_3H_2O_4Ca) + 2H_2O$, dissolves with difficulty in cold water, hence is precipitated by calcium chloride from neutral solutions. Silver nitrate precipitates the *silver salt*, $C_3H_2Ag_2O_4$, as a white, crystalline compound.

The malonic *esters* are obtained by dissolving the acid in alcohol, and conducting HCl-gas into the solution (see above).

The *methyl ester*, $CH_2(CO_2.CH_3)_2$, boils at 175–180°. The *ethyl ester* boils at 195°: its specific gravity at 18° is 1.068. This compound is useful in performing various syntheses (see above). By the action of sodium ethylate upon it the Na-compounds, $CHNa(CO_2.C_2H_5)_2$ and $CNa_2(CO_2.C_2H_5)_2$ (*Berichte*, 17, 2783), result. Upon heating sodium malonic ester to 145° a condensation of 3 molecules occurs, with a splitting off of 3 molecules of alcohol, and there remains the ester of trisod-phloroglucin tricarboxylic acid (a derivative of benzene) (*Berichte*, 18, 3458):—

$$3CHNa(CO_2.C_2H_5)_2 = C_6O_3Na_3(CO_2.C_2H_5)_3 + 3C_2H_5.OH.$$

The amide of malonic acid $(CH_2.(CO.NH_2)_2)$, formed from malonic ester and ammonia, consists of crystals, and melts at 170° (*Berichte*, 17, 133).

Malononitrile,  $CH_2\langle{}^{CN}_{CN}$, methylene cyanide, is obtained by distilling cyanacetamide, $CN.CH_2.CO.NH_2$, with P_2O_5. A crystalline mass, melting at 30° and boiling at 218° C. Silver nitrate precipitates $CAg_2(CN)_2$ from the aqueous solution (*Berichte* 19, Ref. 485).

As in the aceto-acetic esters, so in the malonic esters, the hydrogen of the methylene group (CH_2) can be replaced by alkali metals (p. 400). Malonic ester unites with formaldehyde to produce propantetracarboxylic ester (*Berichte*, 19, 1054). Consult *Berichte*, 20, Refs. 504, 552, upon the action of sodmalonic esters upon unsaturated acids.

When iodine acts upon sodmalonic ester the product is an ester of ethane-tetracarboxylic acid. The disodium compound, under like treatment, would yield ethylene-tetracarboxylic ester, $C_2(CO_2R)_4$.

When nitrous acid is conducted into the solution of the sodium compound of the ethyl ester, **isonitrosomalonic ester**, $C(N.OH)(CO_2.C_2H_5)_2$, is formed. This is a yellow oil which decomposes when heated. Its specific gravity at 15° is 1.149. Saponification with alkalies liberates **isonitrosomalonic acid**, $C(N.OH)(CO_2H)_2$. This is also formed by the action of hydroxylamine (*Berichte*, 16, 608, 1621) upon violuric acid (see this) and mesoxalic acid, $CO(CO_2H)_2$. It is easily soluble in water, crystallizes in shining needles, and melts near 126°, decomposing at the same time into hydrocyanic acid, carbon dioxide and water. **Nitromalonic Ester**, $CH(NO_2)(CO_2.C_2H_5)$, forms when malonic ester dissolves in concentrated nitric acid. It dissolves in ammonia and forms an ammonium salt (*Berichte*, 23, Ref. 62). **Amidomalonic Acid**, $CH(NH_2).(CO_2H)_2$, is obtained from it by reduction with sodium amalgam. This new acid is readily dissolved by water, and when warmed passes into glycocoll, $CH_2(NH_2).CO_2H$ and CO_2. The amide of amidomalonic acid is obtained from chlormalonic ester (*Berichte*, 15, 607).

Chlormalonic Ester, $CHCl(CO_2.C_2H_5)_2$ is obtained by conducting chlorine into warm malonic ethylate. It boils at 222°. When saponified with excess of caustic alkalies it yields oxymalonic acid (tartronic acid), $CH.OH.(CO_2H)_2$. The addition of one molecule of sodium ethylate to its solution produces at first sodium chlormalonic ester, $CNaCl(CO_2R)_2$. The alkylogens convert this into chlorinated alkyl malonic esters (*Berichte*, 13, 2159). The latter yield higher oxydicarboxylic acids, $R.C(OH)(CO_2H)_2$ (*Annalen*, 209, 232), when saponified with excess of caustic alkalies.

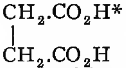
Two molecules of sodium alcoholate convert it into the sodium salt of *chlormalonic acid*, which crystallizes in shining prisms that melt at 133°, and at 180° decompose into CO_2 and monochloracetic acid (*Berichte*, 15, 605).

Monobrom-malonic Acid, $CHBr(CO_2H)_2$, is produced in slight quantity when malonic acid is treated with bromine. It consists of deliquescent needles. Silver oxide converts it into oxymalonic acid (tartronic acid).

Dibrom-malonic Acid, $CBr_2(CO.OH)_2$, is formed when bromine (dissolved in chloroform) is allowed to act upon malonic acid. Deliquescent needles, which melt at 126° and then decompose. Heated with baryta water it changes to dioxymalonic acid (mesoxalic acid).

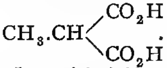
Cyanmalonic Ester, $CH(CN)(CO_2R)_2$, results from the action of cyanogen chloride upon sodium malonic ester (*Berichte*, 20, Ref. 563), or acetyl chloride upon sodium cyanacetic ester. It is a pungent-smelling liquid which boils with decomposition in a vacuum. It has a very acid reaction, and decomposes the alkaline carbonates, forming salts, like $CNa(CN)(CO_2R)_2$ (*Berichte*, 22, Ref. 567).

3. Succinic Acids, $C_4H_6O_4 = C_2H_4\left\langle\begin{array}{l}CO_2H\\CO_2H\end{array}\right.$.



$$\begin{array}{l}CH_2.CO_2H^{*}\\ |\\ CH_2.CO_2H\end{array}$$

Ordinary Succinic Acid.



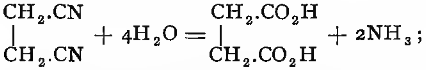
$$CH_3.CH\left\langle\begin{array}{l}CO_2H\\CO_2H\end{array}\right..$$

Isosuccinic Acid.

1. **Succinic Acid**, or ethylene dicarboxylic acid, occurs in amber, in some varieties of lignite, in resins, turpentine oils and in animal fluids. It is formed in the oxidation of fats with nitric acid, in the fermentation of calcium malate or ammonium tartrate and in the alcoholic fermentation of sugar.

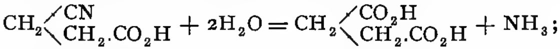
It is synthetically prepared :—

(1) By boiling ethylene cyanide (from ethylene bromide) (p. 303) with alkalies or acids :—



$$\begin{array}{l}CH_2.CN\\ |\\ CH_2.CN\end{array} + 4H_2O = \begin{array}{l}CH_2.CO_2H\\ |\\ CH_2.CO_2H\end{array} + 2NH_3;$$

(2) By converting β-iodpropionic acid (p. 224) into cyanide and decomposing the latter with alkalies or acids :—

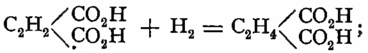


$$CH_2\left\langle\begin{array}{l}CN\\CH_2.CO_2H\end{array}\right. + 2H_2O = CH_2\left\langle\begin{array}{l}CO_2H\\CH_2.CO_2H\end{array}\right. + NH_3;$$

---

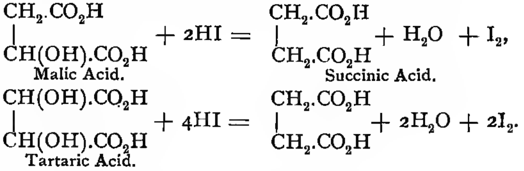
* Considered stereochemically, succinic acid must have the axial-symmetric configuration, $\begin{array}{l}HO_2C.CH_2\\ |\\ CH_2.CO_2H\end{array}$. The plane-symmetric form is unstable, and is only *fixed* in succinic anhydride, $\begin{array}{l}CH_2.CO\\ |\\ CH_2.CO\end{array}\!\!\!>O$.

(3) By the action of nascent hydrogen upon fumaric and maleïc acids:—



$$C_2H_2\left\langle\begin{matrix}CO_2H\\CO_2H\end{matrix}\right. + H_2 = C_2H_4\left\langle\begin{matrix}CO_2H\\CO_2H\end{matrix}\right.;$$

(4) By reducing malic acid (oxysuccinic acid) and tartaric acid (dioxysuccinic acid) with hydriodic acid (p. 41):—



$$\begin{matrix}CH_2.CO_2H\\|\\CH(OH).CO_2H\\\text{Malic Acid.}\end{matrix} + 2HI = \begin{matrix}CH_2.CO_2H\\|\\CH_2.CO_2H\\\text{Succinic Acid.}\end{matrix} + H_2O + I_2,$$

$$\begin{matrix}CH(OH).CO_2H\\|\\CH(OH).CO_2H\\\text{Tartaric Acid.}\end{matrix} + 4HI = \begin{matrix}CH_2.CO_2H\\|\\CH_2.CO_2H\end{matrix} + 2H_2O + 2I_2.$$

Malic acid undergoes a like reduction in the fermentation of its calcium salt.

(5) By the decomposition of aceto-succinic esters (p. 400), and from ethene-tricarboxylic acid by the elimination of carbon dioxide.

Preparation.—Distil amber from an iron retort; evaporate the distillate and purify the residual, brown crystalline mass, by crystallization from dilute nitric acid. The acid is easily prepared by letting calcium malate ferment. Water and rancid cheese are added to crude calcium malate and the mixture let stand at a temperature of 30–40° for several days. Subsequently the succinate of calcium, obtained in this manner, is decomposed with sulphuric acid, the gypsum filtered off and the filtrate evaporated to crystallization. Consult *Berichte*, 14, 214, upon the production of succinic acid by the fermentation of ammonium tartrate.

Succinic acid crystallizes in monoclinic prisms or plates, and has a faintly acid, disagreeable taste. It melts at 180° (185°) and distils at 235°, at the same time decomposing partly into water and succinic anhydride. At the ordinary temperature it dissolves in 20 parts of water. It dissolves with more difficulty in alcohol. Ether will extract nearly all of the acid from its aqueous solution.

Uranium salts decompose aqueous succinic acid in sunlight into propionic acid and CO_2. The galvanic current acts as indicated by the equation (p. 87):—

$$C_2H_4(CO_2H)_2 = C_2H_4 + 2CO_2 + H_2.$$

It (also the alkyl succinic acids) forms fluoresceïn dyes when heated with resorcinol and sulphuric acid.

The salts with the alkali metals are readily soluble in water. The *potassium salt*, $C_4H_4O_4K_2 + 3H_2O$, forms deliquescent needles. The *calcium salt*, $C_4H_4O_4Ca$, separates with 3 molecules of H_2O from a cold solution, but when it is deposited from a hot liquid it contains only $1H_2O$. It dissolves with difficulty in water. When ammonium succinate is added to a solution containing a ferric salt, all the iron is precipitated as reddish-brown basic ferric succinate.

Ethyl Succinic Ester, $C_2H_4(CO_2.C_2H_5)_2$, is obtained in the action of hydrochloric acid upon an alcoholic solution of succinic acid. It is a thick oil, insoluble in water and boils at 216°.

Its specific gravity at 0° is 1.072. Sodium converts it into ethyl succino-succinate.

Methyl Succinic Ester, $C_2H_4(CO_2.CH_3)_2$, has been obtained from silver succinate and methyl iodide, as well as from succinyl chloride and sodium methylate. It melts at 19°, and boils at 80°, under a pressure of 10 mm.

Ethylene Succinic Ester, $C_2H_4\left\langle\begin{matrix}CO_2\\CO_2\end{matrix}\right\rangle C_2H_4$, is produced by heating succinic acid and ethylene glycol to 200°. It fuses at 90°, and decomposes upon distillation.

Succinic Anhydride (succinyl oxide), $C_2H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle O$, is produced in the distillation of succinic acid, or more readily by heating it with 1 molecule of PCl_5; further, by heating succinic acid with acetyl chloride (p. 402). It crystallizes in needles or prisms from alcohol or ether, melts at 120° and distils at 250°. When boiled with water, it reverts to succinic acid.

Two molecules of PCl_5 convert succinic acid into—

Succinyl Chloride, $C_2H_4\left\langle\begin{matrix}CO.Cl\\CO.Cl\end{matrix}\right.$, or $C_2H_4\left\langle\begin{matrix}CCl_2\\CO\end{matrix}\right\rangle O$ (*Berichte*, 22, 3184). This is an oil, solidifying at 0° and boiling at 190°. It forms succinic dimethyl ester with 2 molecules of sodium methylate. By acting with sodium amalgam upon an ethereal solution of succinyl chloride and glacial acetic acid, we get butyrolactone, $C_2H_4\left\langle\begin{matrix}CH_2\\CO\end{matrix}\right\rangle O$ (p. 362), which was formerly considered succinic dialdehyde, $C_2H_4(CHO)_2$.

Zinc ethide converts succinyl chloride into $C_2H_4\left\langle\begin{matrix}C(C_2H_5)_2\\CO\text{———}\end{matrix}\right\rangle O$, γ-diethylbutyrolactone, which boils at 230°; it forms salts of the corresponding acid with alkalies.

Succinamide, $C_2H_4\left\langle\begin{matrix}CO.NH_2\\CO.NH_2\end{matrix}\right.$, is produced by shaking succinic ester with aqueous ammonia. It is a white powder. It is insoluble in water and alcohol, and crystallizes, from hot water, in needles. At 200° it decomposes into ammonia and succinimide.

Ethylene cyanide, $C_2H_4(CN)_2$, (p. 303), is the nitrile of succinic acid.

Succinimide, $C_2H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle NH$. Gentle ignition of the anhydride in a current of dry ammonia or the distillation of ammonium succinate produces this compound. It crystallizes with 1 molecule of H_2O in rhombic plates, and dissolves readily in water and alcohol. It crystallizes from acetone in rhombic octahedra without any water. When anhydrous it melts at 126° and boils at 288°.

Succinimide combines with metallic oxides like those of silver and lead, exchanging its imide hydrogen for metals, for instance, $C_2H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle NAg$. The same compounds are obtained by the double decomposition of the potassium derivative with salts of the heavy metals (*Annalen*, 215, 200). The potassium compound, $C_2H_4(CO)_2NK$ and $C_2H_4(CO)_2K + \frac{1}{2}H_2O$, is formed by adding alcoholic potash to an alcoholic solution of succinimide. Ether precipitates it, either as a powder, or crystalline mass. The *silver salt*, $C_2H_4(CO)_2NAg$ and $C_2H_4(CO)_2NAg + \frac{1}{2}H_2O$, crystallizes in silky needles.

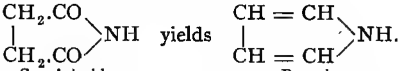
These compounds show that succinimide, like other imides, possesses an acid character.

It is not only the carboxyl group that determines the acid character of the carbon compounds; the imide group, NH, also seems capable of exchanging hydrogen for metals (forming salts), if it be attached to one or two carbonyl groups, CO (as in $CO = NH$, cyanic acid, and in $\begin{matrix}CO\\CO\end{matrix}{>}NH$). This is particularly manifest in the urea derivatives of the dicarboxylic acids (see these).

Methyl Succinimide, $C_2H_4{<}\begin{matrix}CO\\CO\end{matrix}{>}N.CH_3$, is obtained by distilling methylamine succinate. It crystallizes in leaflets, melts at 66.5° and boils at 234°.

Ethyl Succinimide, $C_2H_4{<}\begin{matrix}CO\\CO\end{matrix}{>}N.C_2H_5$, crystallizes in broad needles, which dissolve easily in water, alcohol and ether. It melts at 26° and boils at 234°.

On distilling succinimide with zinc dust, oxygen is withdrawn and pyrrol, C_4H_5N (see this), is formed:—



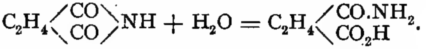
$$\begin{matrix}CH_2.CO\\ |\\ CH_2.CO\end{matrix}{>}NH \text{ yields } \begin{matrix}CH = CH\\ |\\ CH = CH\end{matrix}{>}NH.$$

Succinimide. Pyrrol.

Ethyl Pyrrol, $C_4H_4N(C_2H_5)$, is obtained in a similar manner from ethyl succinimide.

Pyrrolidine, C_4H_9N (*Berichte*, **20**, 2215), is formed in the action of sodium upon succinimide dissolved in absolute alcohol.

Succinamic Acid, $C_2H_4{<}\begin{matrix}CO.NH_2\\CO.OH\end{matrix}$, is produced by heating succinimide with baryta water:—

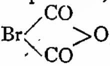


$$C_2H_4{<}\begin{matrix}CO\\CO\end{matrix}{>}NH + H_2O = C_2H_4{<}\begin{matrix}CO.NH_2\\CO_2H\end{matrix}.$$

It is crystalline, and water decomposes it with ease into succinic acid and ammonia.

See *Annalen*, 254, 155, upon the *Chlorsuccinic Acids.*

Mono- and Dibrom-succinic Acids are formed when succinic acid, bromine and water are heated to 150–180° in sealed tubes. The first is the chief product when an excess of water is used. The bromine is more readily introduced into succinic esters, or succinyl chloride, or the anhydride (p. 221). It is not even necessary to use the last two compounds as such; it will suffice to warm the succinic acid with amorphous phosphorus and water (*Berichte*, 21, Ref. 5).

Monobrom-succinic Acid, $C_2H_3Br{<}\begin{matrix}CO_2H\\CO_2H\end{matrix}$, is obtained by the union of fumaric or maleïc acid with HBr($C_4H_4O_4 + HBr = C_4H_5BrO_4$) (*Annalen*, 254, 161). It crystallizes in warty masses, consisting of minute needles, and is readily soluble in water. It melts at 160°, and decomposes into HBr and fumaric acid. It suffers similar decomposition when heated with water. On boiling with moist silver oxide it yields oxysuccinic acid, $C_2H_3(OH)(CO_2H)_2$ (Malic Acid). Its ethyl ester, $C_2H_3Br(CO_2.C_2H_5)_2$, boils at 150–160°, under 50 mm. pressure. With KCN, or when distilled at the ordinary temperature, it forms fumaric ester (*Berichte*, **22**, Ref. 813). Its anhydride,  $C_2H_3Br\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle O$, is produced by heating the acid with acetyl chloride. It melts at 30°. When distilled it decomposes into hydrobromic acid and maleïc anhydride.

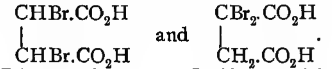
Dibrom-succinic Acid, $C_2H_2Br_2(CO_2H)_2$, results by the direct union of fumaric acid with bromine. It may be obtained by heating succinic acid (12 parts) with bromine (33 parts) and water (12 parts) to 150–180°, until all the bromine has disappeared. It is more easily prepared by heating fumaric acid with bromine and water to 100° C. (*Berichte*, **18**, 676). It consists of prisms which are not very soluble in cold water. When heated to 200–235° it breaks up into HBr and brom-maleïc acid. Boiling water decomposes its salts; the silver salt yields dioxysuccinic acid (inactive tartaric acid), the sodium-salt monobrom-malic acid, $C_2H_2Br(OH)(CO_2H)_2$, and the barium salt, inactive tartaric acid and monobrom-maleïc acid, $C_2HBr(CO_2H)_2$. When dibromsuccinic acid is heated with a solution of potassium iodide it becomes fumaric acid; boiling water decomposes it into HBr and brom-maleïc acid. The *methyl ester*, $C_2H_2Br_2(CO_2.CH_3)_2$, melts at 62°; the *ethyl ester* at 68°, and when distilled it suffers decomposition. It forms fumaric ester when digested with reduced silver.

Isodibrom-succinic Acid, $C_2H_2Br_2(CO_2H)_2$, is isomeric with the preceding. It is obtained in slight quantity by adding bromine to succinic acid, but is better prepared by the addition of Br_2 to maleïc acid (see this), or by digesting the anhydride of the latter with water. It is crystalline and very soluble in water. It melts at 160° and decomposes at 180°, or by boiling with water, into HBr and so-called brom-fumaric acid (p. 425). Silver oxide and water convert it into brom-fumaric and racemic acids (*Berichte*, **21**, 267). Sodium amalgam changes it to succinic acid. When warmed with a solution of potassium iodide it passes into fumaric acid.

The *esters* of this acid are prepared by conducting HCl-gas into the alcoholic solution of the acid. They are liquids, and readily decompose when heated. The anhydride, $C_2H_2Br_2(CO)_2O$, results on heating maleïc anhydride, $C_2H_2(CO)_2O$, to 100° with bromine (dissolved in chloroform). It crystallizes in tables, melts at 42°, and at 100° decomposes into HBr and brom-maleïc anhydride. It readily unites with water to yield isodibrom-succinic acid.

Both dibrom-acids are converted by alcoholic potash into acetylene dicarboxylic acid, $C_2(CO_2H)_2$ (p. 431).

It was generally assumed that the two dibrom-acids were derived from ordinary succinic acid and corresponded to the formulas:—



$$\begin{matrix}CHBr.CO_2H\\ |\\ CHBr.CO_2H\end{matrix} \quad \text{and} \quad \begin{matrix}CBr_2.CO_2H\\ |\\ CH_2.CO_2H\end{matrix}.$$

Dibromsuccinic Acid. Isodibromsuccinic Acid.

Their reactions, however, indicate that both have the first structural formula (*Berichte*, **21**, 264, 788). They, therefore, exhibit the phenomenon of alloisomerism (p. 50), analogous to that of all the other symmetrical disubstituted succinic acids, $\begin{array}{l}CHX.CO_2H\\ |\\ CHX.CO_2H\end{array}$ (p. 419).

Tribrom-succinic Acid, $C_2HBr_3(CO_2H)_2$, is produced when bromine (and water) acts upon brom-maleïc acid and isobrom-maleïc acid; it consists of acicular crystals, which melt at 136-137°. The aqueous solution decomposes at 60° into CO_2, HBr, and dibromacrylic acid, $C_3H_2Br_2O_2$, which melts at 85°.

Sulpho-succinic Acid, $C_2H_3\left\{\begin{array}{l}(CO_2H)_2\\ SO_3H\end{array}\right.$, is obtained by dissolving succinic acid in fuming sulphuric acid, or by the union of fumaric or maleïc acid with primary alkali sulphites. It is tribasic.

Isonitroso-succinic Acid, $\begin{array}{l}C(N.OH).CO_2H\\ |\\ CH_2.CO_2H\end{array}$, oximido-succinic acid. Its ethyl ester is formed by the action of hydroxylamine hydrochloride upon oxalo-acetic ester. It is a colorless oil. Sodium amalgam reduces it to aspartic acid (*Berichte*, 21, Ref. 351). The mono-ethyl ester is obtained from the dinitroso-derivative of succino-succinic ester. It yields ethylic-asparto-ether acid (*Berichte*, 22, Ref. 241).

Di-isonitroso-succinic Acid, $\begin{array}{l}C(N.OH).CO_2H\\ |\\ C(N.OH).CO_2H\end{array}$, is formed by acting upon tetraoxysuccinic acid with hydroxylamine. It crystallizes in prisms and melts with decomposition at 128–130° (*Berichte*, 16, 2985).

Amido-succinic acid (aspartic acid), $C_2H_3(NH_2)(CO_2H)_2$, and amido-succinamic acid (asparagine), $C_2H_3(NH_2)\begin{array}{l}\diagup CO_2H\\ \diagdown CO_2.NH_2\end{array}$, will be described under malic acid, as they bear the same relation to it that glycocoll (amido-acetic) bears to glycollic acid.

Diamido-succinic Acid, $C_2H_2(NH_2)_2\begin{array}{l}\diagup CO_2H\\ \diagdown CO_2H\end{array}$, is formed from dibromsuccinic acid by the action of ammonia, and also results from the diphenylhydrazine derivative of dioxy-tartaric acid through the decomposition brought about by sodium amalgam (*Berichte*, 20, 245):—

$$\begin{array}{l}C(OH)_2.CO_2H\\ |\\ C(OH)_2.CO_2H\end{array}\text{ yields }\begin{array}{l}CH(NH_2).CO_2H\\ |\\ CH(NH_2).CO_2H\end{array}.$$

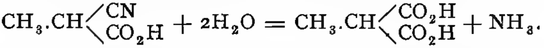
It is almost insoluble in the ordinary reagents, but dissolves in mineral acids and alkalies, with the formation of salts, which are nearly all decomposed by water. It separates from them as a crystalline powder. Rapidly heated, it is almost wholly carbonized. As it contains 2 COOH groups and 2 amide groups, it is a diglycocoll (p. 367).

Another diamido-succinic acid has been described. Its ethyl ester was obtained by the action of alcoholic ammonia upon dibrom-succinic acid (*Berichte*, 15, 1848).

Ethyl Diazo-succinic Ester, $\begin{array}{l}C(N_2).CO_2.C_2H_5\\ |\\ CH_2.CO_2.C_2H_5\end{array}$, is obtained from HCl-ethyl amido-succinic ester (ester of aspartic acid) by the action of sodium nitrite (p. 373). It is a dark-yellow oil, which volatilizes in steam with only partial decomposition. Its reactions show it to be wholly analogous to diazo-acetic ester. When boiled with water it yields nitrogen and fumaric ester. When heated, it sustains a complicated transposition with the formation of the ester of azin-succinic acid (*Berichte*, 18, 1302; 19, 2460). Zinc dust and ammonia convert it into the esters of aspartic acid.

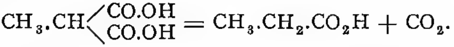
Cyan-succinic Acid, $C_2H_3(CN)(CO_2H)_2$, is produced when potassium cyanide acts upon brom-succinic ester (p. 262). The hydrogen of the CH-group, in its diethyl ester, can be replaced by sodium and alkyls (*Berichte*, 22, Ref. 267).

(2) **Isosuccinic Acid**, $CH_3.CH\Big\langle\begin{matrix}CO_2H\\CO_2H\end{matrix}$, ethidene dicarboxylic acid, methyl malonic acid, is obtained from *α*-chlor- and brom-propionic acids through the cyanide (*Berichte*, 13, 209):—



$$CH_3.CH\Big\langle\begin{matrix}CN\\CO_2H\end{matrix} + 2H_2O = CH_3.CH\Big\langle\begin{matrix}CO_2H\\CO_2H\end{matrix} + NH_3.$$

When ethidene bromide, $CH_3.CHBr_2$, is heated with potassium cyanide and alkalies, we do not obtain ethidene succinic acid by the operation, but ordinary ethylene succinic acid. When malonic esters are treated with sodium and methyl iodide they yield iso-succinic acid. The latter crystallizes in needles or prisms, and is more readily soluble than ordinary succinic acid (in 4 parts H_2O). It sublimes below 100° in plates, melts at 130°, and by further application of heat breaks up into carbon dioxide and propionic acid (p. 351):—



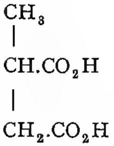
$$CH_3.CH\Big\langle\begin{matrix}CO.OH\\CO.OH\end{matrix} = CH_3.CH_2.CO_2H + CO_2.$$

When heated with water above 100° the result is the same. The *ethyl ester*, $C_4H_4O_4(C_2H_5)_2$, boils at 196°; the *methyl ester* at 179°.

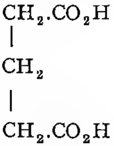
Brom-isosuccinic Acid, $CH_3.CBr(CO_2H)_2$ is formed on heating isosuccinic acid with water and bromine to 100°. Large deliquescent prisms, which decompose readily.

4. Pyrotartaric Acids, $C_5H_8O_4 = C_3H_6\Big\langle\begin{matrix}CO_2H\\CO_2H\end{matrix}$.

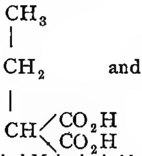
Four of these acids are theoretically possible:—



Pyrotartaric Acid.

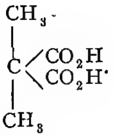


Glutaric Acid.



and

Ethyl Malonic Acid.



Dimethyl Malonic Acid.

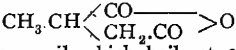
(1) **Pyrotartaric Acid**, $CH_3.CH\Big\langle\begin{matrix}CO_2H\\CH_2.CO_2H\end{matrix}$, propylene dicarboxylic acid, was first obtained in the dry distillation of tartaric

acid (mixed with pumice stone). It may be synthetically prepared from propylene bromide, by means of the cyanide—

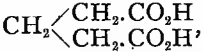
$$CH_3.CH\Big<\begin{matrix}CN\\CH_2.CN\end{matrix}\quad\text{yields}\quad CH_3.CH\Big<\begin{matrix}CO_2H\\CH_2.CO_2H,\end{matrix}$$

or by the action of nascent hydrogen upon the three isomeric acids: ita-, citra-, and mesa-conic acids: $C_5H_6O_4 + H_2 = C_5H_8O_4$. It is further formed from α- and β-methyl aceto-succinic esters (made by introducing methyl into aceto-succinic esters) and by acting on aceto-acetic esters with α-brompropionic esters, p. 400; from β-brombutyric acid by means of the cyanide, and by heating pyroracemic acid, $CH_3.CO.CO_2H$, alone to 170°, or with hydrochloric acid to 100°. The acid consists of small, rhombic prisms, which dissolve readily in water, alcohol and ether. It melts at 112° and when quickly heated above 200°, decomposes into water and the anhydride. If, however, it be exposed for some time to a temperature of 200–210°, it splits into CO_2 and butyric acid. It suffers the same decomposition when in aqueous solution, if acted upon by sunlight in presence of uranium salts.

The neutral *calcium salt*, $C_5H_6O_4Ca + 2H_2O$, dissolves with difficulty in water. The same may be remarked of the *acid potassium salt*, $C_5H_7KO_4$. The *ethyl ester* boils at 218°.



The *anhydride*, $CH_3.CH\Big<\begin{matrix}CO\text{———}\\CH_2.CO\end{matrix}\Big>O$, obtained by heating pyrotartaric acid above 220°, is a heavy oil, which boils at 244.9°, sinks in water and gradually reverts to the acid (*Annalen*, 191, 48).



(2) Glutaric Acid, $CH_2\Big<\begin{matrix}CH_2.CO_2H\\CH_2.CO_2H\end{matrix}$, Normal Pyrotartaric Acid, was first obtained by the reduction of α-oxyglutaric acid with hydriodic acid. It may be synthetically prepared from trimethylene bromide (p. 102), through the cyanide; from aceto-acetic ester by means of the aceto-glutaric ester (p. 400); from glutaconic acid (p. 425), and from propane tetracarboxylic acid, $C_3H_4(CO_2H)_4$, by the removal of $2CO_2$. Glutaric acid crystallizes in large monoclinic plates, melts at 97°, and distils near 303°, with scarcely any decomposition. It is soluble in 1.2 parts water at 14°.

The *calcium salt*, $C_5H_6O_4Ca + 4H_2O$, and *barium salt*, $C_5H_6O_4Ba + 5H_2O$, are easily soluble in water; the first more readily in cold than in warm water. The *ethyl ester*, $C_5H_6O_4(C_2H_5)_2$, boils at 237°. The *anhydride*, $C_5H_6O_3$, forms on slowly heating the acid to 230–280°, and in the action of acetyl chloride on the silver salt of the acid. It crystallizes in needles, melting at 56–57° (after solidification it melts at 36°), and boils near 285°.

Glutarimide, $C_3H_6(CO)_2NH$, results by the distillation of ammonium glutarate. It crystallizes in shining leaflets and melts at 152°.

The vegetable alkaloid piperidine, $C_5H_{10}NH$, is obtained from it by distilling with zinc dust. PCl_5 and HI convert it into the base *pyridine*, C_5H_5N, just as succinimide yields pyrrol (p. 413), (*Berichte*, **16**, 1683).

(3) **Ethyl Malonic Acid**, $C_2H_5.CH\left\langle\begin{matrix}CO_2H\\CO_2H\end{matrix}\right.$, is obtained from *a*-brombutyric ester, through the cyanide, and by the action of Na and C_2H_5I upon malonic ester. It is very similar to ordinary tartaric acid, melts at 111.5° and decomposes at 160°, more rapidly at 170°, into butyric acid and CO_2. The *calcium salt*, $C_5H_6O_4Ca + H_2O$, forms prisms, and is more easily soluble in cold than in hot water. Its *ethyl ester* boils at 200°. For sodium- and chlor-ethyl malonic ester, see *Berichte*, 21, 2085.

(4) **Dimethyl Malonic Acid**, $\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C\left\langle\begin{matrix}CO_2H\\CO_2H\end{matrix}\right.$, is obtained from *a*-bromisobutyric ester by means of potassium cyanide; by introducing methyl into malonic ester, and from mesitylenic acid (*Berichte*, 15, 581). It crystallizes in four-sided prisms, and dissolves with difficulty in alcohol, but is rather readily soluble in water. It is not as soluble as its isomerides. It sublimes about 120° and melts at 170°, decomposing at the same time into CO_2 and isobutyric acid. The *barium salt* crystallizes in needles; the *calcium salt* is more soluble in cold than in warm water. The *ethyl ester* boils at 195°.

The isomeric chlorine and bromine substitution products of the pyrotartaric acids are produced by the direct addition of HCl, HBr and Br_2, to the unsaturated isomeric acids, $C_5H_6O_4$: itaconic, citraconic and mesaconic acids (p. 429). The new derivatives are known as ita-, citra- and mesa-pyrotartaric acids:—

$$\left.\begin{matrix}\text{Itaconic Acid}\\\text{Citraconic Acid}\\\text{Mesaconic Acid}\end{matrix}\right\}C_5H_6O_4 + Br_2 = C_5H_6Br_2O_4\left\{\begin{matrix}\text{Ita-}\\\text{Citra-}\\\text{Mesa-}\end{matrix}\right\}\begin{matrix}\text{Dibrompyro-}\\\text{tartaric acids.}\end{matrix}$$

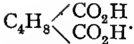
Itachlor-pyrotartaric Acid, $C_5H_7ClO_4$, is formed by heating itaconic acid with fuming hydrochloric acid to 130°. It melts at 145°. When heated with water or alkalies it passes into itamalic acid, $C_5H_7(OH)O_4$. It yields paraconic acid, $C_5H_6O_4$, with silver oxide.

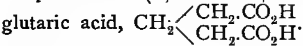
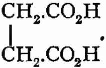
Citra- or Mesa-chlorpyrotartaric Acid is obtained on treating citraconic anhydride with cold concentrated hydrochloric acid, and by heating mesaconic acid to 140° with concentrated hydrochloric acid. It crystallizes in plates and melts at 129°. When boiled with water it breaks up into HCl and mesaconic acid. Boiling alkalies change it into HCl, CO_2 and methacrylic acid, $C_4H_6O_2$.

Fuming hydrobromic acid converts citraconic acid, its anhydride and also mesaconic acid (at 140°) into the same **brompyrotartaric Acid**, $C_5H_7BrO_4$. It melts at 148°, and when boiled with water yields CO_2, HBr and methacrylic acid. **Itabrompyrotartaric Acid**, from itaconic acid, is not so soluble in water, and melts at 137°.

The ita-, citra- and **mesa-dibrompyrotartaric acids**, $C_5H_6Br_2O_4$, are distinguished by their different solubility in water. The ita- compound changes to aconic acid, $C_5H_4O_4$, when the solution of its sodium salt is boiled; the citra- and mesa- compounds, on the other hand, yield brom-methacrylic acid (p. 240).

Nascent hydrogen causes all these substitution derivatives to revert to ordinary pyrotartaric acid.

5. Acids, $C_6H_{10}O_4 =$  $C_4H_8\left\langle\begin{array}{l}CO_2H\\CO_2H\end{array}\right.$

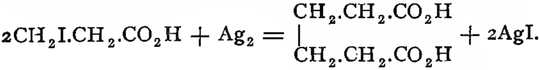
Nine are possible and eight known: (1) Normal Butandicarboxylic acid or Adipic acid. (2) α- and β-Methyl glutaric acids (isomerides), derived from glutaric acid,  $CH_2\left\langle\begin{array}{l}CH_2.CO_2H\\CH_2.CO_2H\end{array}\right.$. (3) Symmetrical and unsymmetrical dimethyl succinic acids and ethyl succinic acid (isomerides) derived from succinic acid,  $\begin{array}{l}CH_2.CO_2H\\|\\CH_2.CO_2H\end{array}$. (4) Propyl, isopropyl and methyl-ethyl malonic acids (isomerides), derived from malonic acid.

Symmetrical dimethyl succinic acid, like other symmetrical disubstituted succinic acids,  $\begin{array}{l}CHX.CO_2H\\|\\CHX.CO_2H\end{array}$ (as dibromsuccinic acid (p. 414), dioxysuccinic acid or tartaric acid, diethyl-, methylethyl-, diisopropyl-, diphenyl-succinic acid, etc.), exists in two modifications. These have the same structural formulas, and are, therefore, to be regarded as alloisomeric (p. 50). In the case of dioxysuccinic or tartaric acid (see this) there are two active and two inactive forms (one capable of division, the other not). They are striking examples of the facts that vant' Hoff endeavors to explain by his theory of *asymmetric* carbon atoms (p. 63). The various dialkyl succinic acids also contain asymmetric carbon atoms, and show some analogy to *para*-tartaric (racemic acid) and *anti-* or *meso*-tartaric acids. On this account their isomerism is presumed to be due to the same cause, and in consequence the modification with the higher melting point, and dissolving with greater difficulty, is known as the *para* form, while the more soluble variety, with lower melting point, is known as the *anti* form (Bischoff, *Berichte*, 20, 2990; 21, 2106). This assumption seems rather questionable, as no one has yet succeeded in converting any of the dialkyl-succinic acids, which are always inactive, into an active form (*Berichte*, 22, 1819).

Another explanation, emphasizing the similarity that may be traced between the two different modifications of the dialkylsuccinic acids and maleïc and fumaric acids, calls the one form "*fumaroid*," and the other "*maleïnoid*" (*Berichte*, 21, 3169). The isomerism is supposed to be due to the same cause that underlies the isomerism of fumaric and maleïc acids. van't Hoff attributes it to the "fixation" of two doubly-linked carbon atoms. This would, then, establish the "fixation" of carbon atoms united by single bonds. The result would be the removal of one of the fundamental ideas of the far-reaching theory of van't Hoff.

A third attempt to elucidate the existing difficulty is known as the "Theory ot dynamical Isomerism" (*Berichte*, 23, 624). It, probably, finds expression in the fact that it seeks to account for isomerides that do not exist (*Berichte*, 23, 1606).

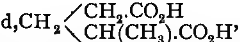
(1) **Adipic Acid**, $C_6H_{10}O_4$, was first obtained by oxidizing fats with nitric acid. It is synthetically prepared by heating β-iodpropionic acid, with reduced silver, to 130–140°:—

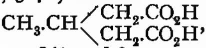


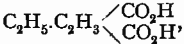
$$2CH_2I.CH_2.CO_2H + Ag_2 = \begin{array}{l}CH_2.CH_2.CO_2H\\|\\CH_2.CH_2.CO_2H\end{array} + 2AgI.$$

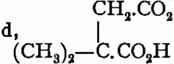
It is also obtained by the action of nascent hydrogen upon hydromuconic acid, $C_6H_8O_4$ (p. 430), and by oxidizing sebacylic acid with nitric acid (along with succinic acid), and by the separation of

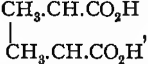
$2CO_2$ from tetramethylene tetracarboxylic acid, $C_4H_6(CO_2H)_4$. It crystallizes in shining leaflets or prisms, which dissolve in 13 parts of cold water, and melt at 148°.

(2) **α-Methyl Glutaric Acid,**$CH_2\left\langle\begin{matrix}CH_2.CO_2H\\CH(CH_3).CO_2H\end{matrix}\right.$, is obtained from methyl aceto-acetic ester, by the action of β-iodpropionic ester and the elimination of ketone (p. 400), by the reduction of saccharon with hydriodic acid, and by the action of KCN upon lævulinic acid. It melts at 76°. It yields methylpenthiophene (*Berichte*, 19, 3270) when heated with P_2S_5.

(3) The β-acid, $CH_3.CH\left\langle\begin{matrix}CH_2.CO_2H\\CH_2.CO_2H\end{matrix}\right.$, from ethidene dimalonic acid (*Annalen*, 218, 161), melts at 86°, and forms an anhydride, which melts at 46° and boils at 283°.

(4) **Ethyl Succinic Acid,** $C_2H_5.C_2H_3\left\langle\begin{matrix}CO_2H\\CO_2H\end{matrix}\right.$, results from ethyl aceto succinic ester, by elimination of ketone, also from α- and β-ethyl ethane tricarbonic ester, $C_2H_5.C_2H_2(CO_2R)_3$, when boiled with sulphuric acid (*Berichte*, 23, 638). It melts at 98°. When heated it yields a liquid anhydride, $C_6H_8O_3$, boiling at 243°.

(5) **Unsymmetrical Dimethyl Succinic Acid,** $\begin{matrix}CH_2.CO_2H\\|\\(CH_3)_2{-}C.CO_2H\end{matrix}$, is produced from isobutylene tricarboxylic acid, $(CH_3)_2.C\left\langle\begin{matrix}CO_2H\\CH(CO_2H)_2\end{matrix}\right.$ (from malonic ester and α-bromiso-butyric acid, *Berichte*, 18, 2350; 23, 636), by splitting off CO_2; when copaïva oil is oxidized (*Berichte*, 18, 3211); and from isobutylene bromide by means of the dicyanide (*Berichte*, 22, 1739). It crystallizes in prisms, melts at 140°, and at higher temperatures, passes into the anhydride, $C_6H_8O_3$, fusing at 29°, and boiling at 230°.

(6) **Symmetrical Dimethyl Succinic Acid,** $\begin{matrix}CH_3.CH.CO_2H\\|\\CH_3.CH.CO_2H\end{matrix}$, exists in two alloisomeric forms, the maleïnoid (*anti-*) form, and the fumaroid (*para-*) modification. These (their esters) are produced as follows: By the elimination of two molecules of carbon dioxide from dimethyl ethane tetracarboxylic acid; by the saponification of αβ-dimethyl-ethane tricarboxylic esters, $(CH_3)_2.C_2H(CO_2R)_3$, with hydrochloric or sulphuric acid (Bischoff, *Berichte*, 22, 389; 23, 639); from αβ-dimethyl aceto succinic ester by the elimination of acid (p. 400); by heating α-brompropionic acid, $CH_3.CHBr.CO_2H$, with reduced silver (*Berichte*, 22, 60), or more readily by the action of potassium cyanide upon α-brompropionic ester (Zelinsky, *Berichte*, 21, 3160); also by the reduction of dimethyl fumaric acid, pyrocinchonic acid (p. 430) with sodium amalgam or hydriodic acid (*Berichte*, 20, 2737; 23, 644). Both symmetrical dimethyl succinic acids are produced in all of these syntheses. They are separated by crystallization from water.

The *para*-acid (analogous to racemic and fumaric acids) is soluble in 96 parts of water at 14°. It forms needles and prisms, melting at 192°–194°. They sustain a partial loss of water upon melting. If the acid be heated for some time to 180°–200°, it yields a mixture of the anhydrides, $C_6H_8O_3$, of the *para-* and *anti* acid. With water each reverts to its corresponding acid. When acetyl chloride acts on the *para*-acid, its *anhydride* is the only product. It crystallizes from ether in rhombic plates, melts at 38°, distils at 234°, and unites with water to form the pure para-acid (*Berichte*, 20, 2741; 21, 3171; 22, 389; 23, 641).

If the *para*-acid be heated to 130° with bromine, it yields pyrocinchonic acid, $C_6H_8O_4$ (p. 430). Both acids, when digested with bromine and phosphorus, yield the same brom-dimethyl succinic acid, $C_6H_9BrO_4$, melting at 91°. Zinc and hydrochloric acid change it to the *anti*-acid (*Berichte*, 22, 66). The *ethyl ester* of the para-acid (from the silver salt) boils at 219°; the *methyl ester* at 199°.

The *anti*-acid (analogous to anti-tartaric acid and maleïc acid) dissolves in 33 parts of water at 14°. It crystallizes in shining prisms, and fuses, after repeated crystallizations from water, at 120–123°. It yields its *anhydride*, $C_6H_8O_3$, when heated to 200°. This melts at 87°. It regenerates the acid with water. If the anti-acid be heated with hydrochloric acid to 190°, it becomes the para-acid. The *methyl ester* boils at 200°; the *ethyl ester* at 222°. When the anti-acid is etherified with HCl, it yields a mixture of the esters of the anti- and para-acid (*Berichte*, 22, 389, 646; 23, 639).

(7) **Methyl-ethyl Malonic Acid,** $\begin{matrix}CH_3\\C_2H_5\end{matrix}\!\!>C(CO_2H)_2$, melts at 118°, and decomposes into CO_2, and methyl-ethyl acetic acid.

(8) **Propyl Malonic Acid,** $C_3H_7.CH(CO_2H)_2$, obtained from malonic acid, and by the reduction of dichloradipic acid (*Berichte*, 18, 852), melts at 96°, and at 150° decomposes into CO_2, and normal valeric acid.

(9) **Isopropyl Malonic Acid,** $C_3H_7.CH<\begin{matrix}CO_2H\\CO_2H\end{matrix}$, from sodium malonic ester, melts at 87°, and at 175° breaks up into CO_2 and normal valeric acid.

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6. Acids, $C_7H_{12}O_4 = C_5H_{10}(CO_2H)_2$.

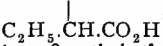
(1) **Normal Pentan-dicarboxylic Acid,** $CH_2<\begin{matrix}CH_2.CH_2.CO_2H\\CH_2.CH_2.CO_2H\end{matrix}$, *a-pimelic acid*, first prepared by oxidizing suberone, $C_7H_{12}O$ (p. 422), by heating furonic acid, $C_7H_8O_5$, with HI, and in the oxidation of fats with nitric acid, can be obtained synthetically from trimethylene bromide and malonic ester by heating pentamethylene tetracarboxylic acid, which is the first product of the reaction (*Berichte*, 18, 3249). It consists of large laminæ or prisms, melting at 102°–104°.

(2) **β-Ethyl Glutaric Acid,** $C_2H_5.CH.<\begin{matrix}CH_2.CO_2H\\CH_2.CO_2H\end{matrix}$, *propylidene diacetic acid*, from propylidene dimalonic acid (from propionic aldehyde and malonic acid) (*Annalen*, 218, 167), melts at 67°.

(3) **Symmetrical Dimethyl Glutaric Acid,** $CH_2<\begin{matrix}CH(CH_3).CO_2H\\CH(CH_3).CO_2H\end{matrix}$, is produced in two alloisomeric forms when methylene iodide acts upon *a*-cyanpropionic ester. These melt at 103° and 128°. The first (regarded as *trimethyl-succinic acid*) has also been obtained from methyl malonic ester and *a*-bromiso-butyric ester (*Berichte*, 22, 2823; 23, 1600). Symmetrical diphenyl glutaric acid has been prepared in but one variety (*Berichte*, 22, 3289).

(4) **Propyl Succinic Acid,** $C_3H_7.CH<\begin{matrix}CH_2.CO_2H\\CO_2H\end{matrix}$, from propyl-ethylene tricarboxylic ester (*Annalen*, 214, 54), crystallizes in warty masses, and melts at 91°.

(5) **Isopropyl Succinic Acid,** $(CH_3)_2.CH.CH<\begin{matrix}CH_2.CO_2H\\CO_2H\end{matrix}$, Pimelic Acid, was first prepared by fusing camphoric acid, and may be synthetically obtained from aceto-acetic or malonic esters (*Berichte*, 16, 2622; *Annalen*, 220, 271). It forms crusts, is readily soluble in water, alcohol and ether, melts at 114°, and on stronger heating, yields an anhydride, boiling at 250°.

(6) **Methyl Ethyl Succinic Acid,**  $\begin{matrix}CH_3.CH.CO_2H\\|\\C_2H_5.CH.CO_2H\end{matrix}$, exists in two alloisomeric modifications. It results after heating *aβ*-methyl-ethyl ethylene tricarboxylic ester with sulphuric acid. The *para*-acid melts at 168°, and when heated for

some time passes into the anhydride of the anti-variety. The *anti-* or *meso*-acid melts at 84°, and yields a liquid anhydride, boiling at 243°.

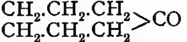
(7) **Normal Butyl Malonic Acid,** $C_4H_9.CH(CO_2H)_2$, has been obtained from α-bromcaproic acid and potassium cyanide. It melts at 101°, and at 140° decomposes into CO_2 and caproic acid.

(8) **Isobutyl Malonic Acid,** $(CH_3)_2.CH.CH_2.CH(CO_2H)_2$, from malonic ester, melts at 107°.

(9) **Diethyl Malonic Acid,** $(C_2H_5)_2C(CO_2H)_2$, from ethyl malonate, melts at 121°, and above 170°, decomposes into CO_2 and diethyl acetic acid.

7. **Acids,** $C_8H_{14}O_4 = C_6H_{12}(CO_2H)_2$.

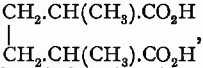
(1) **Suberic Acid,** $C_8H_{14}O_4$, probably of normal structure, is obtained by boiling corks, or fatty oils, with nitric acid (*Berichte,* 13, 1165). It is soluble in 200 parts of cold water, readily in hot water, alcohol and ether. It crystallizes in needles or plates, melting at 140° and subliming without decomposition. Its *ethyl ester* boils at 280–282°. *Hexane,* C_6H_{14}, and *Suberone,* $C_7H_{12}O$ =



$$\begin{matrix}CH_2.CH_2.CH_2\\CH_2.CH_2.CH_2\end{matrix}\!>\!CO$$

(*Annalen,* 211, 117), result when its calcium salt is distilled. Suberone is a liquid boiling at 180°. Its odor resembles that of peppermint.

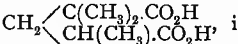
(2) *aa*-**Dimethyl Adipic Acid,**



$$\begin{matrix}CH_2.CH(CH_3).CO_2H\\|\\CH_2.CH(CH_3).CO_2H\end{matrix}$$

, has been prepared by the action of reduced silver upon β-bromisobutyric acid. It occurs in two alloisomeric modifications. One melts at 139°, the other is a liquid (*Berichte,* 23, 295).

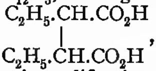
(3) **Trimethyl Glutaric Acid,**



$$CH_2\!\begin{matrix}\diagup C(CH_3)_2.CO_2H\\\diagdown CH(CH_3).CO_2H\end{matrix}$$

, is formed, together with tetramethyl succinic acid (p. 423), when α-bromisobutyric acid is heated with reduced silver. It melts at 97° and sublimes without decomposition. It is not volatile with steam. When the acid is heated for some time, or acted upon with acetyl chloride, it changes to its *anhydride,* $C_8H_{12}O_3$, melting at 96°, and boiling at 262° (*Berichte,* 23, 300).

(4) **Symmetrical Diethyl Succinic Acid,**

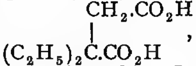


$$\begin{matrix}C_2H_5.CH.CO_2H\\|\\C_2H_5.CH.CO_2H\end{matrix}$$

, exists, like other symmetrical dialkylsuccinic acids, in two alloisomeric modifications (p. 419). These are obtained: By the elimination of $2CO_2$ from diethylethane-tetracarboxylic acid, $(C_2H_5)_2C_2(CO_2H)_4$ (*Berichte,* 21, 2085); by heating xeronic anhydride (p. 431) with hydriodic acid (*Berichte,* 20, Ref. 416; 21, 2105). The diethyl ester results upon heating α-brombutyric ester with silver (Hell, *Berichte,* 22, 67), and upon boiling *aβ*-diethyl-ethane-tricarboxylic ester, $(C_2H_5)_2C_2H(CO_2R)_3$, with sulphuric acid (*Berichte,* 21, 2089; 23, 650). The *para-acid* is soluble in 162 parts of water at 23°. It crystallizes in needles and melts about 189–192°. It then loses water. The *anti-acid* is soluble in 41 parts of water at 23°, and melts at 129°. Heated to 240° the anti-acid forms a liquid *anhydride,* $C_8H_{12}O_3$, boiling at 246°, and reverting to the acid when treated with water. The para-acid, after long heating at 240°, also yields the anhydride of the anti-acid. *Vice-versâ,* the *anti*-acid is changed to the para-acid when heated to 200° with hydrochloric acid or water, (*Berichte,* 21, 2102; 23, 656).

There is a third diethylsuccinic acid. It is supposed to be symmetrical (*Berichte,* 23, 628). It melts at 137.5°. It is very probably ethyl-methyl-glutaric acid (*Berichte,* 23, 1606).

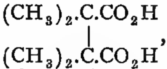
(5) **Unsymmetrical Diethyl Succinic Acid,**



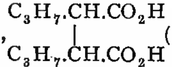
$$\begin{matrix}CH_2.CO_2H\\|\\(C_2H_5)_2C.CO_2H\end{matrix}$$

, has been obtained from α-diethyl-ethane-tricarboxylic ester. It melts at 86°. It forms an anhydride, boiling about 71° (*Berichte,* 23, 651).

For two additional *ethyl-dimethyl-succinic acids,* see *Berichte,* 23, 1606.

(6) **Tetramethyl Succinic Acid,**  $\begin{array}{l}(CH_3)_2.C.CO_2H\\ \quad\quad\;|\\ (CH_3)_2.C.CO_2H\end{array}$, is formed, together with trimethyl glutaric acid (p. 422), when α-bromisobutyric acid (or its ethyl ester) is heated with silver. It is volatile with steam. It melts about 190–192°. It parts quite readily with water and passes into the **anhydride**, $C_8H_{12}O_3$, melting at 147°, and boiling at 230° (*Berichte*, 23, 297).

(7) **n-Pentyl Malonic Acid,** $C_5H_{11}.CH(CO_2H)_2$, from brom-œnanthylic ester and potassium cyanide, melts at 82°. It decomposes above 129° and splits off CO_2.

Symmetrical Diisopropyl Succinic Acid,  $\begin{array}{l}C_3H_7.CH.CO_2H\\ \quad\quad\;|\\ C_3H_7.CH.CO_2H\end{array}$ (?), appears in two alloisomerides when α-bromisovaleric acid, $C_3H_7.CHBr.CO_2H$, is acted upon with silver. The one variety volatilizes with steam and melts at 178°. It readily passes into an oily anhydride on heating. The other is non-volatile, melts at 197°, and sublimes undecomposed above 210° (*Berichte*, 22, 48).

Higher dibasic acids are produced by oxidizing the fatty acids or oleic acids with nitric acid. They always form succinic and oxalic acids at the same time. The acids of the series, $C_nH_{2n-4}O_2$ (p. 244), usually decompose into the acids $C_nH_{2n}O_4$, when oxidized with fuming nitric acid. The mixture of acids that results is separated by fractional crystallization from ether; the higher members, being less soluble, separate out first (*Berichte*, 14, 560).

Lepargylic Acid, $C_9H_{16}O_4$, **Azelaic Acid,** is best prepared by oxidizing castor oil (*Berichte*, 17, 2214). It crystallizes in shining leaflets, resembling benzoic acid. It melts at 106°, and dissolves in 100 parts of cold water.

Sebacic Acid, $C_{10}H_{18}O_4$, is obtained by the dry distillation of oleic acid, by the oxidation of stearic acid and spermaceti, and by fusing castor oil with caustic potash. It crystallizes in shining laminæ, which melt at 127°.

Brassylic Acid, $C_{11}H_{20}O_4$, obtained by oxidizing behenoleic and erucic acids, melts at 108°, and is almost insoluble in water.

Roccellic Acid, $C_{17}H_{32}O_4$, occurs free in *Roccella tinctoria.* Prisms melting at 132°.

Cetyl Malonic Acid, $C_{19}H_{36}O_4 = C_{16}H_{33}.CH(CO_2H)_2$, from malonic ester and cetyl iodide, melts at 121°, and immediately breaks down into CO_2 and stearic acid.

UNSATURATED DICARBOXYLIC ACIDS, $C_nH_{2n-4}O_4$.

The acids of this series bear the same relation to those of the oxalic acid series that the acids of the acrylic series bear to the fatty acids. They can be obtained from the saturated dicarboxylic acids by the withdrawal of two hydrogen atoms. This is effected by acting on the monobrom-derivatives with alkalies:—

$$\underset{\text{Bromsuccinic Acid.}}{C_2H_3Br(CO_2H)_2} + KOH = \underset{\text{Fumaric Acid.}}{C_2H_2(CO_2H)_2} + KBr + H_2O;$$

or, the same result is reached by letting potassium iodide act upon the dibrom-derivatives (p. 235). Thus, fumaric acid is formed from both dibrom- and isodibrom-succinic acids :—

$$C_2H_2Br_2(CO_2H)_2 + 2KI = C_2H_2(CO_2H)_2 + 2KBr + I_2;$$

and mesaconic acid, $C_3H_4(CO_2H)_2$, from citra- and mesa-dibrom-pyrotartaric acids, $C_3H_4Br_2(CO_2H)_2$. As a general thing the unsaturated acids are obtained from the oxydicarboxylic acids by the elimination of water (p. 235).

The esters of these acids are obtained in the condensation of malonic esters with aldehydes :—

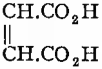
$$CH_3.CHO + CH_2(CO_2R)_2 = CH_3.CH{:}C(CO_2R)_2 + H_2O.$$

Ethidene malonic esters are formed at the same time; from them we can get saturated dicarboxylic acids (*Annalen*, 218, 156).

The union is more easily brought about by the action of sod-malonic ester (*Berichte*, 20, Ref. 258, 552).

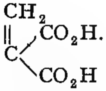
The isomerisms of the acids of this series offer peculiar relations, as yet unexplained. The lowest member of the series has the formula $C_2H_2(CO_2H)_2$. This can be structurally represented in two ways:—

(1)



$$\begin{array}{l} CH.CO_2H \\ \| \\ CH.CO_2H \end{array}$$

and (2)

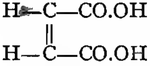


$$\begin{array}{l} CH_2 \\ \|\quad CO_2H. \\ C \\ \quad CO_2H \end{array}$$

The first would correspond to succinic acid, the second to the iso-acid. Two acids—maleïc and fumaric—with the formula $C_2H_2(CO_2H)_2$, are known. Owing to its ability to form an anhydride, maleïc acid is supposed to have the first structural formula. (The supposition that a divalent carbon atom is present in the acid offers no explanation for its behavior.) The second formula is then ascribed to fumaric acid. Certain synthetic methods (p. 425) used in forming these acids argue for the preceding views. Yet most of the transpositions suffered would seem to show that the acids have the same structural formula.

This is evidently a case of alloisomerism (p. 50), which our present structural formulas fail to represent. Various hypotheses have been advanced for the explanation of the peculiar isomerism of these two acids (*Annalen*, 239, 161), but have, to some extent, been abandoned, *e.g.*, the supposition that the relations existing between the acids (fumaric and maleïc) were similar to those existing between racemic and inactive tartaric acid, has been disproved by a determination of the molecular weight according to Raoult (Paternò, *Berichte*, 21, 2156). Another suggestion is that the isomerism is due to a difference of structure in the two carboxyl groups, and that maleïc acid should be viewed as a dioxylactone (*ibid.*). A more promising indication for the solution of these difficulties, seems to lie in the introduction of representations upon the spatial relations of the atoms in accordance with the view or hypothesis of LeBel and van't Hoff, lately elaborated by J. Wislicenus (see pp. 51, 52, and (*Berichte*, 20, Ref. 448; 21, Ref. 501).

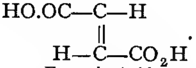
This view ascribes to fumaric acid the axial-symmetric, and to maleïc acid the plane-symmetric configuration, briefly represented as follows:—



$$\begin{array}{l} H-C-CO.OH \\ \quad\;\, \| \\ H-C-CO.OH \end{array}$$

Maleïc Acid.

and



$$\begin{array}{l} HO.OC-C-H \\ \qquad\quad\;\; \| \\ \qquad\;\; H-C-CO_2H \end{array}.$$

Fumaric Acid.

The arrangement of the two carboxyls upon the same (corresponding) side gives maleïc acid the power of forming an anhydride. In fumaric acid the carboxyls oppose each other; an anhydride cannot be formed.

1. **Fumaric and Maleïc Acids,** $C_2H_2{<}\begin{smallmatrix}CO_2H\\CO_2H\end{smallmatrix}$, are obtained by distilling malic acid:—

$$C_2H_3(OH)(CO_2H)_2 = C_2H_2(CO_2H)_2 + H_2O;$$

fumaric acid remains in the residue, while maleïc acid and its anhydride pass over into the receiver (*Berichte*, **12**, 2281). The last two are formed in especially large quantities on rapidly heating malic acid, whereas, by prolonged heating at 140°–150°, fumaric acid is the chief product (*Berichte*, **18**, 676). If maleïc acid be heated for some time at 130° it changes to fumaric acid; when the latter is distilled it decomposes into water and maleïc anhydride. Maleïc acid is only completely converted into fumaric acid when it is heated, either alone, or in aqueous solution, to 200–201°, in a sealed tube. Fumaric acid is fully changed to maleïc anhydride by heating to 160° with P_2O_5 (Tanatar). For the conversion of maleïc into fumaric acid, by means of bromine and hydrobromic acid, consult *Berichte*, **21**, Ref. 501, and *Annalen*, **248**, 342. Acetylene is obtained by the electrolysis of a concentrated solution of the sodium salts of the two acids (p. 87).

We can obtain maleïc acid (its ester) synthetically by heating dichloracetic ester, $CHCl_2.CO_2.C_2H_5$, with silver or sodium. Fumaric acid is formed from $\alpha\beta$-dichlorpropionic acid (which yields α-chloracrylic acid, $CH_2{:}CCl.CO_2H$, p. 237), by the action of potassium cyanide and caustic potash. Both syntheses indicate that the first formula properly falls to maleïc acid and the second to fumaric (p. 424). This conclusion is contradicted by the formation of maleïc acid from β-dibrompropionic acid (which yields α bromacrylic acid, $CH_2{:}CBr.CO_2H$, p. 237), by the action of potassium cyanide and potash, and fumaric acid from chlorethenyl tricarboxylic ester, $C_2H_2Cl(CO_2.C_2H_5)_3$ (*Berichte*, 13, 100 and 2163); also, by the fact that fumaric acid is formed from dichloracetic and malonic acids (*Annalen*, 218, 169). The action of sodium ethylate upon α-bromisobutyric acid produces α-ethoxy-isosuccinic acid (see Isomalic Acid). β-Ethoxy-isosuccinic ester and methylene malonic ester are produced by the interaction of methylene iodide and sodium malonic ester.

Fumaric Acid occurs free in many plants, in Iceland moss, in *Fumaria officinalis* and in some fungi. It is produced by heating dibrom- and isodibrom-succinic acids with a solution of potassium iodide; and from monobrom- and sulpho-succinic acids by fusion with potash. It may be prepared by boiling brom-succinyl chloride with water (*Berichte*, 21, Ref. 5). It is almost insoluble in water. Mineral acids precipitate it from solutions of its alkali salts as a white crystalline powder. It crystallizes from hot water in small, striated prisms. It has a very acid taste, and dissolves readily in alcohol and ether. It melts with difficulty, sublimes at 200°, forming maleïc anhydride and water. Sodium amalgam, hydriodic acid and other reducing agents convert it into succinic acid. Metallic zinc combines with fumaric acid in the presence of water, forming zinc succinate: $C_4H_4O_4 + Zn = C_4H_4O_4Zn$.

Fuming hydrobromic acid at 100° converts fumaric into monobromsuccinic acid. At ordinary temperatures it combines with bromine (and water) very slowly, more rapidly on heating to 100°, yielding dibromsuccinic acid. When fumaric acid (also maleïc acid, *Berichte*, 18, 2713) is heated with caustic soda to 100°, or with water to 150–200°, it passes into inactive malic acid, which, at 135°, decomposes into water and maleïc acid. The esters of fumaric and maleïc acids pass into alkyloxysuccinic acids (*Berichte*, 18, Ref. 536) when heated with sodium alcoholates. On oxidizing the acid with MnO_4K it yields racemic, whereas, maleïc acid forms inactive tartaric acid (*Berichte*, 14, 713).

With the exception of the alkali, all the salts of fumaric acid dissolve with difficulty in water. The *silver salt*, $C_4H_2O_4Ag_2$, is perfectly insoluble; hence, silver nitrate will completely precipitate fumaric acid from even dilute solutions.

The *esters* are obtained from the silver salt by the action of alkyl iodides, and by leading HCl into the alcoholic solutions of fumaric and maleïc acids (*Berichte*, 12, 2283). They are also produced in the distillation of the esters of brom-succinic acid, malic acid and aceto-malic acid (*Berichte*, 22, Ref. 813). They unite just as readily as the esters of maleïc acid with 2Br (forming esters of dibromsuccinic acid).

The *methyl ester*, $C_2H_2(CO_2.CH_3)_2$, forms white needles, melting at 102°, and boiling at 192°. The *ethyl ester* is liquid, and boils at 218°. It can be obtained by the action of PCl_3 upon esters of malic acid.

Maleïc Acid crystallizes in large prisms or plates, is very easily soluble in cold water, and possesses a peculiar taste. It melts at 130° and distils at 160°, decomposing partially into the anhydride and water. Heated for some time at 130°, or boiled with dilute sulphuric acid, or nitric acid, with HBr and HI, it changes to fumaric acid. Nascent hydrogen converts it into ordinary succinic acid. Metallic zinc dissolves in aqueous maleïc acid without evolving hydrogen, and forms zinc maleate and acid zinc succinate:—

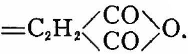
$$3C_4H_4O_4 + 2Zn = C_4H_2O_4Zn + (C_4H_4O_4)_2H_2Zn.$$

Fuming hydrobromic acid combines with maleïc acid at 0° and yields monobromsuccinic acid; an equivalent of fumaric acid forms at the same time. Bromine (and water) at ordinary temperatures converts the acid into isodibrom-succinic and fumaric acids.

The *esters* are produced in the same manner as those of the preceding acid. Traces of iodine will change them, on warming, into esters of fumaric acid. The latter also result in conducting HCl-gas into the alcoholic solutions of maleïc acid. Bromine converts them into esters of dibrom-succinic acid; fumaric acid very probably appears at first.

The *methyl ester*, $C_2H_2(CO_2.CH_3)_2$, is a liquid, and boils at 205°. The *ethyl ester* boils at 225°.

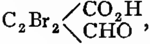
Maleïc anilide separates when aniline acts upon aqueous maleïc acid. All the derivatives of this acid react similarly, while fumaric acid and its derivatives do not enter such a combination (*Berichte*, 19, 1375. Compare *Annalen*, 239, 137).

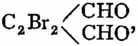
Maleïc Anhydride—Maleyl Oxide, $C_4H_2O_3$= $C_2H_2\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle O$.

This is produced by distilling maleïc or fumaric acid, or more readily by heating maleïc acid with acetyl chloride (p. 402); it is purified by crystallization from chloroform (*Berichte*, 12, 2281, and 14, 2546). It consists of needles or prisms, which melt at 53° (60°) and boil at 202° (196°). It regenerates maleïc acid by union with water, and forms isodibromsuccinic anhydride when heated with bromine to 100°.

Brom-maleïc Acid, $C_4H_3BrO_4$, is produced by boiling barium dibromsuccinate or the free acid with water. It consists of prisms, melting at 128°. **Brom-fumaric Acid**, $C_4H_3BrO_4$, called isobrommaleïc acid, is formed, the same as the preceding, from isodibromsuccinic acid, or its barium salt, or by the addition of HBr to acetylene dicarboxylic acid (p. 431). It consists of very soluble leaflets, which melt at 179°.

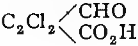
These two brom-acids conduct themselves toward bromine and HBr the same as maleïc and fumaric acids. When boiled with HBr brommaleïc acid is converted into bromfumaric acid; its esters, too, change to those of bromfumaric acid when they are heated with iodine. Sodium amalgam changes both to fumaric and subsequently to succinic acid. By distillation, both yield water and brommaleïc anhydride, C_4HBrO_3. The latter readily unites with water, forming brommaleïc acid (*Annalen*, 195, 56).

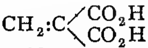
Dibrom-maleïc Acid, $C_2Br_2(CO_2H)_2$, is obtained by acting on succinic acid with Br, or by the oxidation of mucobromic acid with bromine water, silver oxide or nitric acid. It is very readily soluble, melts at 120°–125°, and readily forms the *anhydride*, $C_2Br_2(CO)_2O$, which melts at 115°, and sublimes in needles (*Berichte*, 13, 736). Its half-aldehyde is the so-called **mucobromic acid**, $C_4H_2Br_2O_3$=  $C_2Br_2\left\langle\begin{matrix}CO_2H\\CHO\end{matrix}\right.$, which results from the action of bromine water upon pyromucic acid. It crystallizes in glistening laminæ, and melts at 120°. When oxidized it is converted into dibrom-maleïc acid; baryta changes it to malonic, dibrom-acrylic and brompropiolic acids.

The *dialdehyde* of dibrom-maleïc acid,  $C_2Br_2\left\langle\begin{matrix}CHO\\CHO\end{matrix}\right.$, is produced when bromine water acts upon dibrompyromucic acid, $C_2H_2Br_2O_3$. It melts at 88°, and when oxidized yields mucobromic acid.

Dichlormaleïc Acid, $C_2Cl_2(CO_2H)_2$. Its *imide*,  $\begin{matrix}CCl.CO\\ \| \\ CCl.CO\end{matrix}{>}NH$, is obtained when the perchlorpyrocoll and succinimide (p. 412) are heated in a current of chlorine. It consists of needles melting at 179°. Boiling caustic potash converts the imide into dichlormaleïc acid. This consists of deliquescent needles, which on the application of heat pass into the *anhydride*, $C_2Cl_2(CO)_2O$, which melts at 120°. When the imide is heated with water CO_2 splits off and *a*-dichloracrylic acid is produced (*Berichte*, 16, 2394; 17, 553). Potassium nitrite converts the imide into an analogue of nitranilic acid (*Berichte*, 22, 33).

PCl_5 converts succinic chloride into two isomeric *dichlormaleïc chlorides*, C_4Cl_6O, from which the acid and anhydride can be obtained (*Berichte*, 18, Ref. 184).

The half-aldehyde of dichlormaleïc acid is the so-called **mucochloric acid**,  $C_2Cl_2{<}\begin{matrix}CHO\\CO_2H\end{matrix}$. This is obtained when chlorine water acts upon pyromucic acid. It melts at 125°. Alkalies convert it into formic and *a*-dichloracrylic acid.

Methylene Malonic Acid,  $CH_2{:}C{<}\begin{matrix}CO_2H\\CO_2H\end{matrix}$ (p. 424), is hypothetical and isomeric with fumaric and maleïc acids. It cannot be obtained free. Its *diethyl ester*, $C_4H_2O_4(C_2H_5)_2$, is produced when 1 molecule of methylene iodide and 2 molecules of sodium ethylate act upon 1 molecule of malonic ethyl ester (together with β-ethoxy iso-succinic ester, $C_2H_5.O.CH_2.CH(CO_2R)_2$ (*Berichte*, 23, 194; 22, 3294). Under diminished pressure it distils as a mobile, badly-smelling oil. If allowed to stand, it soon changes to a white, solid mass, $(C_8H_{12}O_4)_2$. The liquid ester deports itself like an unsaturated compound. It unites with bromine. When saponified with alcoholic potash it takes up alcohol and becomes β-ethoxy-isosuccinic acid, $C_2H_5.O.CH_2.CH(CO_2H)_2$.

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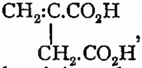
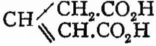
2. Acids, $C_5H_6O_4 = C_3H_4(CO_2H)_2$.

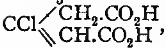
Six unsaturated dicarboxylic acids of this formula are known: ethidene malonic, methylene succinic, glutaconic, itaconic, citraconic and mesaconic acid; the structure of the last three is yet in doubt. The so-called *vinylmalonic acid*, obtained from ethylene bromide and the ester of malonic acid, is identical with *a*-trimethylene dicarboxylic acid, derived from trimethylene.

Ethidene Malonic Acid, $CH_3.CH{:}C(CO_2H)_2$, is only known in its ethyl ester. This is formed by the condensation of malonic ester with acetaldehyde on heating with acetic anhydride (p. 424). It boils at 220°, and at 118–120° under a pressure of 21 mm. When saponified with baryta water it yields an oxydicarboxylic acid, $C_3H_5(OH)(CO_2H)_2$. It combines with malonic ester on heating, and becomes ethidene dimalonic ester.

The condensation of malonic ester with chloral may be effected by heating them with acetic acid anhydride, the product being the diethyl ester of *Trichlor ethidene malonic acid*, $CCl_3.CH{:}C(CO_2H)_2$, a thick oil, boiling about 160° under 23 mm. pressure.

Methylene Succinic Acid,  $\begin{matrix}CH_2{:}C.CO_2H\\ | \\ CH_2.CO_2H\end{matrix}$, is probably β-trimethylene dicarboxylic acid (see this), inasmuch as it is produced from malonic ester and *a*-bromacrylic ester (*Berichte*, 20, Ref. 47).

Glutaconic Acid,  $CH{<}\begin{matrix}CH_2.CO_2H\\CH.CO_2H\end{matrix}$, arises in the saponification of the dicarboxy-glutaconic ester (obtained from the ester of malonic ester and chloroform, *Annalen*, 222, 249). It melts at 132°. Sodium amalgam converts it into glutaric acid.

PCl_5 converts acetone dicarboxylic acid (p. 435) into **Chlorglutaconic Acid**,  $CCl\begin{matrix}\diagup CH_2.CO_2H\\ \diagdown\!\!\diagdown CH.CO_2H\end{matrix}$, melting at 129°, and when acted upon by alcoholic potash, passing into glutinic acid (p. 432) (*Berichte*, 20, 147).

Citraconic and itaconic acids, judging from their behavior, bear the same relations to mesaconic acid that maleïc sustains to fumaric acid. They yield anhydrides, whereas mesaconic acid when distilled passes into citraconic anhydride.

Citraconic and itaconic acids are obtained in the distillation of citric acid. Aconitic acid, $C_3H_3(CO_2H)_3$ (see this), is produced at first and by the subsequent withdrawal of water and CO_2 it yields itaconic and citraconic anhydrides: $C_6H_6O_6 = C_5H_4O_3 + H_2O + CO_2$. Both anhydrides are present in the filtrate. The first yields itaconic acid by union with water (*Berichte*, 13, 1541.) When free itaconic acid is distilled it yields water and citraconic anhydride, which changes to the acid on warming with water. If citraconic acid be heated for some time to 100° or its aqueous solution to 130°, itaconic acid is produced. Boiling dilute nitric acid or concentrated haloid acids convert citraconic into mesaconic acid.

Citra-, ita- and mesaconic acids unite with chlorine, bromine and the halogen hydrides, yielding derivatives of pyrotartaric acid (p. 416); the first two acids react in the cold; mesaconic acid (like fumaric acid) only on the application of heat. Nascent hydrogen converts them all into the same pyrotartaric acid. The electrolysis of their sodium salts (p. 87) decomposes them, according to the equation:—

$$C_3H_4(CO_2H)_2 = C_3H_4 + 2CO_2 + H_2,$$

when ordinary allylene, $CH_3.C\vdots CH$, results from citra- and itaconic acid, and iso-allylene (p. 89) from itaconic acid.

Citraconic Acid, $C_5H_6O_4$, is obtained from its anhydride by heating the latter with water. It crystallizes in glistening prisms, which deliquesce in the air, and melt at 80°. It breaks up by distillation into its anhydride and water. **Citraconic Anhydride**, $C_5H_4O_3$, is also formed by heating the acid with acetyl chloride, and is obtained by the repeated distillation of the distillate (see above) resulting from citric acid. It is an oily liquid which boils at 213–214° with partial transformation into xeronic anhydride (see below); it combines to citraconic acid when heated with water.

Itaconic Acid, $C_5H_6O_4$, is best obtained by heating citraconic anhydride with 3–4 parts water to 150°. It crystallizes in rhombic octahedra, dissolves in 17 parts of H_2O at 10°, melts at 161° and decomposes when distilled into citraconic anhydride and water. Itaconic acid gives the maleïc acid reaction with aniline (p. 427 and *Berichte*, 19, 1383). **Itaconic Anhydride**, $C_5H_4O_3$, is prepared from the acid on heating with acetyl chloride (*Berichte*, 13, 1541). It crystallizes from chloroform in rhombic prisms, melts at 68° and distils unaltered under diminished pressure, but at ordinary pressures changes to citraconic anhydride. It dissolves in water with formation of itaconic acid.

Mesaconic Acid, $C_5H_6O_4$, is prepared by heating citra- and itaconic acid with a little water to 200° and may be obtained by evaporating citraconic anhydride with dilute nitric acid (*Annalen*, 188, 73). It dissolves with difficulty in water (47 parts at 18°), crystallizes in glistening needles or prisms, melts at 202° and at 205° decomposes into citraconic anhydride and water.

Consult *Berichte*, 14, 2785, for the esters of citra-, ita-, and mesaconic acids.

3. **Acids,** $C_6H_8O_4 = C_4H_6(CO_2H)_2$.*

Allyl Malonic Acid, $CH_2:CH.CH_2.CH(CO_2H)_2$, is obtained from malonic ester by means of allyl iodide. It crystallizes in prisms and melts at 103° (*Annalen*, 216, 52). Hydrobromic acid converts it into carbovalerolactonic acid, $C_6H_8O_8$ (the lactone of γ-oxyproprio-malonic acid) (p. 352):—

The latter is a thick liquid, readily soluble in water. When heated to 200° it breaks up into CO_2 and valerolactone (p. 363).

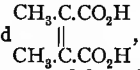
Propylidene Malonic Acid, $C_2H_5.CH:C(CO_2H)_2$, is produced by the action of malonic acid upon propionic aldehyde. It breaks down into carbon dioxide and propylidene acetic acid (p. 241), when distilled.

Hydromuconic Acid exists in a stable and an unstable modification (*Berichte*, 23, Ref. 231):—

$$CO_2H.CH_2.CH:CH.CH_2.CO_2H \text{ and } CO_2H.CH_2.CH_2.CH:CH.CO_2H.$$

Unstable or Δβγ-acid. Stable or Δαβ-acid.

The *unstable* variety is formed in the reduction of dichlormuconic acid, or of muconic acid (p. 432), and of diacetylene dicarboxylic acid (p. 432). It dissolves with difficulty in cold water. It melts at 195°. Potassium permanganate dissolves it to form malonic acid. If boiled with sodium hydroxide it is transformed into the *stable* acid. The latter melts at 169°. Potassium permanganate converts it into succinic acid. Sodium amalgam reduces the unstable acid, after its conversion into the stable variety, to adipic acid.

Dimethyl Fumaric Acid or Maleïc Acid  $\begin{array}{l} CH_3.C.CO_2H \\ \quad\| \\ CH_3.C.CO_2H \end{array}$, pyrocinchonic acid, is only known in its salts and ethers. When separated from the latter it is at once transformed into the anhydride, $C_6H_6O_3$. The latter is obtained by oxidizing turpentine oil (together with terebic acid), by heating cinchonic acid, $C_7H_6O_5$, (with separation of CO_2), and by heating α-dichlor-, or dibrom-propionic acid, $CH_3.CBr_2.CO_2H$, with reduced silver (*Berichte*, 18, 826, 835). The anhydride crystallizes from water in large pearly laminæ, which melt at 96° and distil at 223°. The aqueous solution has a very acid reaction and decomposes alkaline carbonates. The salts have the formula, $C_6H_6O_4Me_2$; its solutions acquire a dark-red color on the addition of ferric chloride. It is oxidized by a chromic acid mixture, and yields 2 molecules of acetic acid and 2 molecules of carbon dioxide. By the action of sodium amalgam, or by heating with hydriodic acid it is converted into unsymmetrical dimethylsuccinic acid (p. 420) (*Berichte*, 18, 838). Pyrocinchonic acid, like malic acid, unites with metallic zinc (*Berichte*, 18, 844). Consult *Berichte*, 23, Ref. 92, upon *methylitaconic* and *methylcitraconic acids.*

4. **Acids,** $C_7H_{10}O_4 = C_5H_8(CO_2H)_2$.

Allyl Succinic Acid,  $C_3H_5.CH\left\langle\begin{array}{l} CH_2.CO_2H \\ CO_2H \end{array}\right.$, results by the withdrawal of carbon dioxide from allyl ethenyl tricarboxylic acid, $C_3H_5.C_2H_2(CO_2H)_3$ (*Berichte*, 16, 335). It crystallizes from alcohol in leaflets, melts at 94° and when

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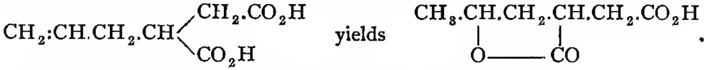
* Tetramethylene dicarboxylic acid is isomeric with these unsaturated acids.

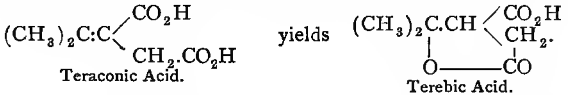
heated above 140° passes into the corresponding anhydride, $C_7H_8O_3$—an oil boiling near 250°. Hydrobromic acid converts it into **Carbocaprolactonic Acid,** $C_7H_{10}O_4$, the lactone of γ-oxypropio-succinic acid :—



$$CH_2{:}CH.CH_2.CH\begin{cases}CH_2.CO_2H\\CO_2H\end{cases} \quad \text{yields} \quad \begin{array}{l}CH_3.\underset{|}{C}H.CH_2.\underset{|}{C}H.CH_2.CO_2H\\ \quad\;\; O\text{———}CO\end{array}.$$

The latter melts at 69° and distils at 260° without decomposition.

Teraconic Acid, $(CH_3)_2C{:}C\begin{smallmatrix}CO_2H\\CH_2.CO_2H\end{smallmatrix}$, is produced in small quantity (together with pyroterebic acid) (p. 241) in the distillation of terebic acid (*Annalen*, 208, 50), and may be prepared by the action of sodium upon terebic esters (*Annalen*, 220, 254). It melts at 162°, decomposing at the same time into water and its anhydride, $C_7H_8O_3$. The latter boils near 275° and by its union with water regenerates teraconic acid. Hydrobromic acid or heat and sulphuric acid cause it to change to isomeric terebic acid (a lactonic acid, see this) (*Annalen*, 226, 363):—



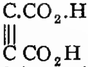
$$(CH_3)_2C{:}C\begin{cases}CO_2H\\CH_2.CO_2H\end{cases} \quad \text{yields} \quad \begin{array}{l}(CH_3)_2\underset{|}{C}.CH\begin{cases}CO_2H\\ \underset{|}{C}H_2.\end{cases}\\ \qquad\;\; O\text{———}CO\end{array}$$

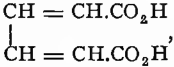
Teraconic Acid. Terebic Acid.

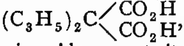
5. **Xeronic Acid,** $C_8H_{12}O_4$, or **Diethyl Fumaric Acid,** $\begin{array}{c}C_2H_5.C.CO_2H\\ \|\\ C_2H_5.C.CO_2H\end{array}$ (*Berichte*, 15, 1321), is very much like dimethyl fumaric acid, and when it is freed from its salts it immediately decomposes into water and the anhydride, $C_8H_{10}O_3$. The latter is produced in the distillation of citraconic anhydride, and is an oil which is not very soluble in water. It boils at 242°. It volatilizes in a current of steam. It is also obtained from α-dibrombutyric acid, $C_2H_5.CBr_2.CO_2H$, when heated with silver (*Annalen*, 239, 276). If it is heated with hydriodic acid it suffers reduction to diethylsuccinic acid (p. 422).

DIBASIC ACIDS, $C_nH_{2n-6}O_4$.

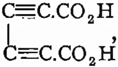
Acetylene Dicarboxylic Acid, $C_4H_2O_4 = \begin{array}{l}C.CO_2H\\ |||\\ C.CO_2H\end{array}$, is obtained when alcoholic potash is allowed to act upon dibrom- and isodibrom-succinic acid (*Berichte*, 18, 677; 21, Ref. 658). It crystallizes with two molecules of water, but these escape on exposure. The anhydrous acid crystallizes from ether in thick plates, and melts with decomposition at 175°. The acid unites with the haloid acids to form halogen fumaric acids, $C_4H_3XO_4$ (p. 427). Its esters unite with bromine and form dibrommaleïc esters. With water they yield oxalacetic acid (*Berichte*, 22, 2929). The primary *potassium salt*, C_4HKO_4, is not very soluble in water and when heated decomposes into CO_2 and potassium propiolate (p. 244). Traces of acetylene are produced at the same time. Phenylhydrazine converts acetylene dicarbonic ester directly into the phenylhydrazone of oxalacetic ester (p. 435).

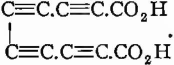
Glutinic Acid,  $\begin{array}{l}C.CO_2.H\\ |||\\ C\ CO_2H\end{array}$, is obtained by the action of alcoholic potash upon chlorglutaconic acid (p. 429). It crystallizes from water in minute needles, melting at 145–146° with evolution of carbon dioxide. This gas is also liberated when the acid is boiled with water.

Muconic Acid,  $\begin{array}{l}CH = CH.CO_2H\\ |\\ CH = CH.CO_2H\end{array}$, is formed when alcoholic potash acts upon the dibromide of $\beta\gamma$-hydromuconic acid (p. 430). It melts above 260°. *Dichlormuconic Acid*, $C_6H_4Cl_2O_4$, results when PCl_5 acts upon mucic acid. It yields $\beta\gamma$-hydromuconic acid with sodium amalgam (*Berichte*, 23, Ref. 232).

Diallyl Malonic Acid,  $(C_3H_5)_2C\begin{array}{l}\diagup CO_2H\\ \diagdown CO_2H\end{array}$, is obtained from malonic ester. It melts at 133°. Hydrobromic acid converts it into the corresponding *dilactone*, which melts at 106° (*Annalen*, 216, 67). When heated it breaks up into CO_2 and diallyl acetic acid (p. 245).

Unsaturated Acids:—

Diacetylene Dicarboxylic Acid, $C_6H_2O_4$ =  $\begin{array}{l}C\equiv C.CO_2H\\ |\\ C\equiv C.CO_2H\end{array}$, is made by the action of potassium ferricyanide upon the copper compound of propiolic acid (*Berichte*, 18, 678, 2269). It dissolves quite readily in water, alcohol and ether, crystallizes in needles or plates with 1 molecule H_2O, instantly assumes a dark red color on exposure to light, and at 177° explodes with a loud report. Sodium amalgam reduces it to hydromuconic acid, then to adipic acid and at the same time splits it up into propionic acid. The *ethyl ester* is an oil boiling at 184° under a pressure of 200 mm. Zinc and hydrochloric acid decompose it and yield propargylic ethyl ether, $CH\equiv C.CH_2.O.C_2H_5$ (p. 136), compare p. 244.

Tetra-acetylene Dicarboxylic Acid, $C_{10}H_2O_4$ =  $\begin{array}{l}C\equiv C.C\equiv C.CO_2H\\ |\\ C\equiv C.C\equiv C.CO_2H\end{array}$. CO_2 escapes on digesting the acid sodium salt of diacetylene dicarboxylic acid with water, and there is formed the sodium salt of *diacetylene monocarboxylic acid*, which cannot be obtained in a free condition. When ferricyanide of potassium acts upon the copper compound of this acid tetra-acetylene dicarboxylic acid is formed. This crystallizes from ether in beautiful needles, rapidly darkening on exposure to light and exploding violently when heated (*Berichte*, 18, 2271). Consult *Berichte*, 18, 2277, for an experiment made to explain the explosibility of this derivative.

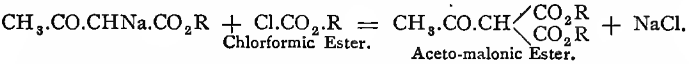
KETONE DICARBOXYLIC ACIDS.

In this class are included the dibasic acids, which contain ketone groups in addition to the two carboxyl groups. They may be synthesized in the following manner:—

1. By introducing acid radicals into malonic ester. This is done by acting upon the sodium compounds with acid chlorides:—

$$CH_3.COCl + CHNa(CO_2.R)_2 = \underset{\text{Aceto-malonic ester.}}{CH_3.CO.CH(CO_2R)_2} + NaCl.$$

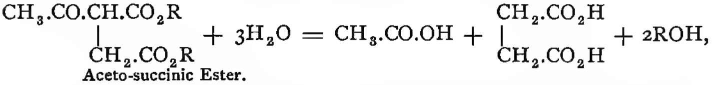
2. By the introduction of acid residues into aceto-acetic ester. In this case esters of the fatty acids are allowed to act upon the sodium derivatives (p. 342):—



$$\mathrm{CH_3.CO.CHNa.CO_2R} + \underset{\text{Chlorformic Ester.}}{\mathrm{Cl.CO_2.R}} = \underset{\text{Aceto-malonic Ester.}}{\mathrm{CH_3.CO.CH}\langle\begin{smallmatrix}\mathrm{CO_2R}\\ \mathrm{CO_2R}\end{smallmatrix}} + \mathrm{NaCl}.$$

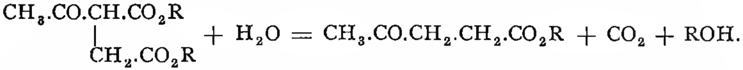
Chloracetic ester, $CH_2Cl.CO_2.R$, under like conditions, yields acetosuccinic ester, while β-iodo-propionic ester forms acetoglutaric ester, etc. Many other dibasic acids are produced in an analogous manner (*Annalen*, **216**, 39, 127).

The β-ketone dicarboxylic acids, formed as above, sustain the same decompositions as the β-ketone monocarboxylic acids (p. 333). Thus, acetosuccinic ester when acted upon with concentrated potassium hydroxide, breaks down into acetic and succinic acids (acid decomposition):—



$$\underset{\text{Aceto-succinic Ester.}}{\begin{array}{l}\mathrm{CH_3.CO.CH.CO_2R}\\ \quad\quad |\\ \quad\quad \mathrm{CH_2.CO_2R}\end{array}} + 3\mathrm{H_2O} = \mathrm{CH_3.CO.OH} + \begin{array}{l}\mathrm{CH_2.CO_2H}\\ |\\ \mathrm{CH_2.CO_2H}\end{array} + 2\mathrm{ROH},$$

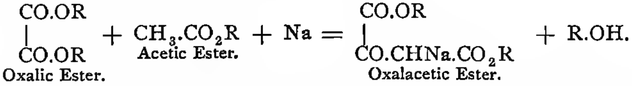
whereas, if boiled with baryta water, or acids, the ketone decomposition occurs, and the products are CO_2, and β-acetopropionic acid (lævulinic acid):—



$$\begin{array}{l}\mathrm{CH_3.CO.CH.CO_2R}\\ \quad\quad |\\ \quad\quad \mathrm{CH_2.CO_2R}\end{array} + \mathrm{H_2O} = \mathrm{CH_3.CO.CH_2.CH_2.CO_2R} + \mathrm{CO_2} + \mathrm{ROH}.$$

Both decompositions occur simultaneously, as in the case of aceto-monocarboxylic ester.

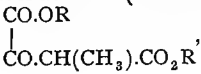
3. By the condensation of oxalic ester and fatty acid esters through the action of sodium or sodium alcoholate. This is analogous to the formation of aldehydic and ketonic esters (*W. Wislicenus*, *Berichte*, **19**, 3325; **20**, 3392):—



$$\underset{\text{Oxalic Ester.}}{\begin{array}{l}\mathrm{CO.OR}\\ |\\ \mathrm{CO.OR}\end{array}} + \underset{\text{Acetic Ester.}}{\mathrm{CH_3.CO_2R}} + \mathrm{Na} = \underset{\text{Oxalacetic Ester.}}{\begin{array}{l}\mathrm{CO.OR}\\ |\\ \mathrm{CO.CHNa.CO_2R}\end{array}} + \mathrm{R.OH}.$$

The sodium compounds are first formed. The esters are obtained by heating them with acids.

The esters of all the fatty acids having primary radicals (carboxyl attached to a CH_2-group, *e. g.*, propionic acid, normal butyric acid), act like the acetic esters. Isobutyric acid does not react (*Berichte*, **21**, 1156). Propionic ester yields methyl oxalacetic ester,

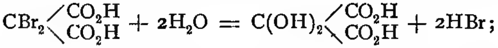


$$\begin{array}{l}\mathrm{CO.OR}\\ |\\ \mathrm{CO.CH(CH_3).CO_2R}\end{array},$$

etc.

In the same way oxalic and lævulinic esters yield oxal-lævulinic ester (*Berichte*, **22**, 885), and oxalic and succinic esters yield oxal-succinic ester—a ketone tricarboxylic acid.

1. Mesoxalic Acid, $C_3H_2O_5 = CO(CO_2H)_2$ or $C_3H_4O_6 = C(OH)_2.(CO_2H)_2$, dioxymalonic acid, is formed from amidomalonic acid by oxidation with iodine in an aqueous solution of potassium iodide; from dibrom-malonic acid by boiling with baryta water or silver oxide:—



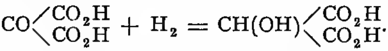
$$CBr_2\left\langle\begin{matrix}CO_2H\\CO_2H\end{matrix}\right. + 2H_2O = C(OH)_2\left\langle\begin{matrix}CO_2H\\CO_2H\end{matrix}\right. + 2HBr;$$

and by boiling alloxan (mesoxalyl urea) with baryta water.

Preparation.—Add barium alloxanate (5 gr.) to water (1 litre) of 80°, then quickly heat to boiling (5–10 minutes) and filter. As the solution cools, barium mesoxalate will separate in the form of a fine, crystalline powder. It is decomposed with an equivalent quantity of sulphuric acid, the barium sulphate removed by filtration, and the solution concentrated at a temperature of 40–50°, until the remaining mesoxalic acid solidifies in a crystalline mass.

Mesoxalic acid crystallizes in deliquescent prisms containing 1 molecule H_2O; it melts at 115° without loss of water, and at higher temperatures decomposes into CO_2 and glyoxylic acid, $CHO.CO_2H$. It breaks up into CO and oxalic acid by the evaporation of its aqueous solution.

As mesoxalic acid contains 1 molecule of water intimately combined, and as all its salts dried at 110° contain 1 molecule H_2O, it is considered a dihydroxyl derivative—dioxymalonic acid, $C(OH)_2.(CO_2H)_2$. Here, as in the case of glyoxylic acid, we observe an intimate union of two OH groups with 1 carbon atom, already combined with negative CO_2H groups (p. 331). Again, mesoxalic acid deports itself like a ketonic acid (p. 329), inasmuch as, with a loss of water, it unites with primary alkaline sulphites, and when acted upon by sodium amalgam in an aqueous solution of 90°, it is changed to tartronic acid:—



$$CO\left\langle\begin{matrix}CO_2H\\CO_2H\end{matrix}\right. + H_2 = CH(OH)\left\langle\begin{matrix}CO_2H\\CO_2H\end{matrix}\right..$$

It combines with hydroxylamine to isonitrosomalonic acid (p. 409). With phenylhydrazine it forms the phenylhydrazone, $C(N.NHC_6H_5)(CO_2H)_2$. This is identical with benzene malonic acid obtained by the action of benzene diazo-salts upon malonic acid (*Berichte*, **21**, 118).

Barium mesoxalate, $C(OH)_2\left\langle\begin{matrix}CO_2\\CO_2\end{matrix}\right\rangle Ba$, and calcium mesoxalate, are crystalline powders, not very soluble in water. The *ammonium salt*, $C(OH)_2.(CO_2.NH_4)_2$, obtained by evaporating a solution of the acid in ammonium carbonate, crystallizes in needles. The *silver salt*, $C(OH)_2.(CO_2Ag)_2$, is a white amorphous powder, which blackens on exposure to the air, and when boiled with water affords mesoxalic acid, silver oxalate, silver and CO_2.

The *diethyl ester*, $C(OH)_2(CO_2.C_2H_5)_2$, is obtained by the action of C_2H_5I upon the silver salt. It is an unstable oil. It forms a crystalline diamide, $C(OH)_2.(CO.NH_2)_2$, with aqueous ammonia. Acetyl chloride converts it into the *diacetyl compound*, $C(O.C_2H_3O)_2\left\langle\begin{array}{l}CO_2.C_2H_5\\CO_2.C_2H_5\end{array}\right.$ (p. 196), which crystallizes in long needles, melting at 145°.

2. **Oxalo-Acetic Acid,** $C_4H_4O_5 = \begin{array}{l}CO.CO_2H\\|\\CH_2.CO_2H\end{array}$. The diethyl ester (analogous to acetoacetic ester, p. 431) is formed when sodium acts upon a mixture of oxalic and acetic esters, and when acetylene dicarboxylic ester is digested with sulphuric acid. The ester is a thick oil. Heat soon decomposes it. When boiled with alkalies it breaks down into alcohol, oxalic and acetic acids. Boiling H_2SO_4 causes it to undergo the ketone decomposition (p. 337) whereby CO_2 and pyroracemic acid ($CH_3.CO.CO_2H$) are produced. Ferric chloride imparts a deep red color to the solution of the ester.

Oxalo-acetic acid is both an *α*- and *β*-ketonic acid (331). The union of the ester with phenylhydrazine gives rise to a condensation product—a pyrazolon-derivative (*Berichte*, 22, 2929).

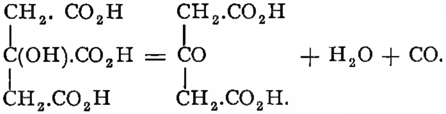
The phenylhydrazine derivative of amido-oxalo-acetic acid, $\begin{array}{l}C(N_2H.C_6H_5).CO_2H\\|\\CH(NH_2).CO_2H\end{array}$, has been prepared by the reduction of the osazone of dioxytartaric acid (*Berichte*, 20, 245).

Bromine converts oxalo-acetic ester into the dibromide, $C_4H_2Br_2O_5$. This undergoes decomposition quite readily (*Berichte*, 22, 2912).

3. Acids, $C_5H_6O_5$.

(1) **Aceto-malonic Acid,** $CH_3.CO.CH(CO_2H)_2$. Its ethyl ester is formed when chlorcarbonic ester acts upon sodium aceto-acetic ester (*Berichte*, 22, 2617; 21, 3567). It is a mobile liquid, boiling about 240°. It decomposes into CO_2, acetone and acetic acid when saponified.

2. **Acetone Dicarboxylic Acid,** $CO\left\langle\begin{array}{l}CH_2.CO_2H\\CH_2.CO_2H\end{array}\right.$, may be obtained by warming citric acid with sulphuric acid:—

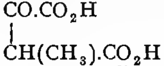


$$\begin{array}{l}CH_2.CO_2H\\|\\C(OH).CO_2H\\|\\CH_2.CO_2H\end{array} = \begin{array}{l}CH_2.CO_2H\\|\\CO\\|\\CH_2.CO_2H.\end{array} + H_2O + CO.$$

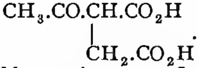
Dehydrated citric acid is heated upon a water bath with 2 parts concentrated sulphuric acid until the evolution of CO ceases and that of CO_2 begins. The rapidly cooled mass is then mixed with 2½ parts water, when the acid separates as a crystalline mass. To obtain the diethyl ester the product of the above reaction is at once poured into absolute alcohol (*Berichte*, 17, 2542; 18, Ref. 468).

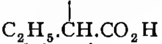
Acetone dicarboxylic acid dissolves readily in water and ether; it crystallizes in colorless needles, melting at 130° when it decomposes into CO_2 and acetone. The same alteration occurs on boiling the acid with water, acids or alkalies; aceto-acetic ester is also an intermediate product. The solutions of the acid are colored violet by ferric chloride. Being a ketonic acid it unites with phenylhydrazine; with HCN it yields an oxy-cyanide (p. 202), which is reconverted into citric acid by hydrochloric acid. The *diethyl ester*, $C_5H_4(C_2H_5)_2O_5$ (preparation above) is an oily liquid, which can only be distilled under reduced pressure. The 4H-atoms of the two CH_2-groups in it can be successively replaced by alkyls (*Berichte*, 18, 2289).

PCl_5 converts the acid into chlorglutaconic acid (p. 429). Ammonia and the diethyl ester combine to form oxyamidoglutaminic ester (*Berichte*, 18, 2290), which condenses further to glutazine (see this)—a trioxypyridine derivative (*Berichte*, 19, 2694). The esters of acetone dicarboxylic acid condense with anilines to form esters of oxyquinoline carboxylic acids. Phenylhydrazine yields derivatives of oxy-quinizine (-pyrazole) (*Berichte*, 18, Ref. 469). Metallic sodium causes the ester to condense to dioxyphenylaceto-dicarboxylic ester (*Berichte*, 19, 1446).

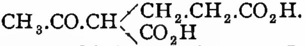
(2) **Methyl Oxal-acetic Acid,**  $\begin{array}{l}CO.CO_2H\\ |\\ CH(CH_3).CO_2H\end{array}$, α-oxal-propionic acid. Its ethyl ester is obtained from the esters of oxalic and propionic acids. It is a colorless oil. Its alcoholic solution is colored an intense red by ferric chloride. It decomposes into alcohol, oxalic and propionic acids when boiled with alkalies. By the ketone decomposition (boiling with sulphuric acid) it separates into CO_2, and propionyl carboxylic acid, $CH_3.CH_2.CO.CO_2H$ (p. 342) (*Berichte*, 20, 3394).

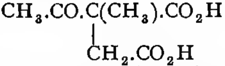
4. Acids, $C_8H_8O_5$.

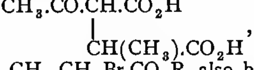
(1) **Aceto-succinic Acid,**  $\begin{array}{l}CH_3.CO.CH.CO_2H\\ \qquad\quad |\\ \qquad\quad CH_2.CO_2H\end{array}$. Its ethyl ester is prepared from aceto-acetic ester and chlor-acetic ester. It boils at 244–250°. Ferric chloride does not color it. By the acid decomposition it yields acetic and succinic acids; by the ketone decomposition the products are CO_2, and β aceto-propionic acid (p. 343). The hydrogen atom of the CH-group, in the esters, can be replaced by alkyls with the formation of alkyl-aceto-succinic acids (see below).

(2) **Ethyl Oxal-acetic Acid,**  $\begin{array}{l}\qquad CO.CO_2H\\ \qquad |\\ C_2H_5.CH.CO_2H\end{array}$, α-oxal-butyric acid, is obtained as ethyl ester from oxalic and butyric esters. Isobutyric ester does not react (p. 434).

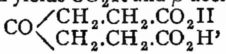
5. Acids, $C_7H_{10}O_5$.

(1) **Aceto-glutaric Acid,**  $CH_3.CO.CH\begin{array}{l}\diagup CH_2.CH_2.CO_2H.\\ \diagdown CO_2H\end{array}$ Its ethyl ester is formed from aceto-acetic ester, and β-iodopropionic ester. It yields acetic and glutaric acids in the acid decomposition.

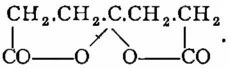
(2) *α*-**Methyl Aceto-succinic Acid,**  $\begin{array}{l}CH_3.CO.C(CH_3).CO_2H\\ \qquad\quad |\\ \qquad\quad CH_2.CO_2H\end{array}$. Its methyl ester is formed from methyl aceto-acetic ester and chloracetic ester; also by methylating aceto-succinic ester. It boils at 263°. The acid decomposition converts it into methyl succinic acid and acetic acid, while by the ketone decomposition (separation of CO_2R) the product is β-aceto-butyric acid (p. 344).

(3) *β*-**Methyl Aceto-succinic Acid,**  $\begin{array}{l}CH_3.CO.CH.CO_2H\\ \qquad\quad |\\ \qquad\quad CH(CH_3).CO_2H\end{array}$, from aceto-acetic ester and α-brom-propionic ester, $CH_3.CH_2Br.CO_2R$, also boils at 263°,

and in the acid decomposition breaks down into methyl-succinic acid and acetic acid. The ketone decomposition yields CO_2R and β-aceto-isobutyric acid (p. 344).



(4) **Acetone-diacetic Acid,** $CO\left\langle\begin{array}{l}CH_2.CH_2.CO_2H\\CH_2.CH_2.CO_2H\end{array}\right.$, loses water and becomes the γ-dilactone, $C_7H_8O_4$:—



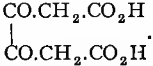
This is formed when succinic acid is boiled for some time:—

$$2C_4H_6O_4 = C_7H_8O_4 + CO_2 + 2H_2O$$

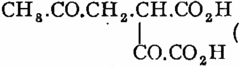
(*Berichte*, 22, 681). It melts at 75°, and distils without decomposition under reduced pressure. Boiling water, or better, boiling alkalies cause it to become *acetone diacetic acid*, by absorption of water. This acid is identical with *propion-dicarboxylic acid*, and *hydrochelidonic acid*. The first is obtained by the action of HCl upon furfur-acrylic acid, and the latter by the reduction of chelidonic acid.

Acetone-diacetic acid melts at 143°. Acetyl chloride or acetic anhydride will again convert it into the γ-dilactone. Hydroxylamine changes it to the *oxime*, $C(N.OH)(C_2H_4.CO_2H)_2$, melting at 129°. Its *phenylhydrazone*, $C(N_2H.C_6H_5)(C_2H_4.CO_2H)_2$, melts at 107° (*Berichte*, 22, 682).

Diketone-dicarboxylic Acids :—

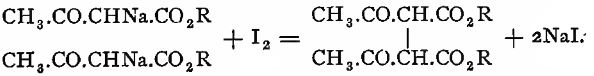


1. **Oxal-diacetic Acid,** $C_6H_6O_6 = \begin{array}{l}CO.CH_2.CO_2H\\|\\CO.CH_2.CO_2H\end{array}$. Its ethyl ester, like oxal-acetic ester (p. 435), is produced in the action of sodium upon a mixture of oxalic ester with two molecules of acetic ester, (*Berichte*, 20, 591); also from oxalic ester and chlor-acetic ester by the action of zinc (*Ketipic Acid*, *Berichte*, 20, 202). It consists of leafy crystals, melting at 77°. Ferric chloride imparts an intense red color to its alcoholic solution. Concentrated hydrochloric acid sets free the oxaldiacetic acid. This is a white insoluble powder. When heated it yields, 2 CO_2, and diacetyl (p. 326). Chlorine and bromine convert the ester into *tetrachlor-* and *tetrabrom-oxaldiacetic ester*. The first is called *tetrachlordiketo-adipic ester*, and is also produced when chlorine acts upon dioxyquinone dicarboxylic ester (*Berichte*, 20, 3183).



2. **Oxal-lævulinic Acid,** $C_7H_8O_6 = \begin{array}{l}CH_3.CO.CH_2.CH.CO_2H\\\quad\quad\quad\quad\quad\quad|\\\quad\quad\quad\quad\quad CO.CO_2H\end{array}$ (?). The ethyl ester results from the action of sodium or sodium ethylate upon oxalic and lævulinic esters. It is a thick oil. Ferric chloride colors its alcoholic solution an intense red. Cupric acetate precipitates the copper salt from an alcoholic solution (*Berichte*, 21, 2583).

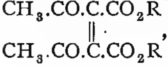
3. **Diaceto-succinic Acid,** $C_8H_{10}O_6$. Iodine converts sod-aceto-acetic ester (2 molecules) into its ethyl ester (*Annalen*, 201, 144):—



$$\begin{array}{l}CH_3.CO.CHNa.CO_2R\\\\CH_3.CO.CHNa.CO_2R\end{array} + I_2 = \begin{array}{l}CH_3.CO.CH.CO_2R\\\quad\quad\quad\quad|\\CH_3.CO.CH.CO_2R\end{array} + 2NaI.$$

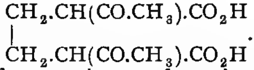
It crystallizes in thin plates and melts at 78°. It is very unstable. It undergoes various re-arrangements, in accord with its γ-diketonic nature (with the atomic group—CO.CH.CH.CO—). Thus, when heated or when acted upon by acids, it yields carbopyrotritartaric ester (a derivative of furfurol). Pyrrol derivatives result when it is acted upon with ammonia and amines. This reaction will serve for the detection of diaceto-succinic ester (*Berichte*, 19, 14). Phenylhydrazone produces dipyrazolon derivatives (*Annalen*, 238, 168).

Sodium hydroxide causes the ester to break down into $2CO_2$, and acetonyl acetone (p. 328).

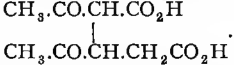


Iodine, acting upon disod-diaceto-succinic ester, produces *diaceto-fumaric ester*, $\begin{array}{l} CH_3.CO.C.CO_2R \\ \quad\;\; \| \\ CH_3.CO.C.CO_2R \end{array}$, melting at 96°.

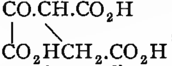
Analogues of Diacetosuccinic Acid:—



Diaceto-adipic Acid, $\begin{array}{l} CH_2.CH(CO.CH_3).CO_2H \\ | \\ CH_2.CH(CO.CH_3).CO_2H \end{array}$. Ethylene bromide acting upon two molecules of sodacetoacetic ester, forms its diethyl ester (*Berichte*, 19, 2045). Phenylhydrazine converts it into a dipyrazolon-derivative (*Berichte*, 19, 2045).

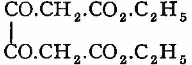


Diaceto-glutaric Acid, $\begin{array}{l} CH_3.CO.CH.CO_2H \\ \qquad\qquad | \\ CH_3.CO.CH.CH_2CO_2H \end{array}$. Its ester is obtained from aceto-acetic ester and from lævulinic ester (p. 343). Being a γ-diketone compound it unites with ammonia and forms a pyrrol-derivative (*Berichte*, 19, 47).



Oxal-succinic Acid, $C_6H_6O_7 = \begin{array}{l} CO.CH.CO_2H \\ | \quad \diagdown \\ CO_2H\,CH_2.CO_2H \end{array}$, is an analogous ketone tricarboxylic acid. Its ethyl ester forms when sodium ethylate acts upon oxalic ester and succinic ester. When its dilute solutions are digested, oxalic and lævulinic acids are produced. Being a β-ketonic acid derivative, its ester yields a pyrazolon compound with phenylhydrazine (*Berichte*, 22, 885).

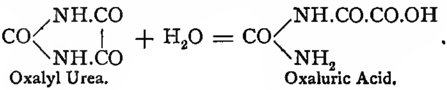
When metallic sodium is permitted to act upon a mixture of oxalic ester, with two molecules of acetic ester, the product will be—



Oxalyl-diacetic Ester, $\begin{array}{l} CO.CH_2.CO_2.C_2H_5 \\ | \\ CO.CH_2.CO_2.C_2H_5 \end{array} = C_{10}H_{14}O_6$. This is a leafy crystalline mass, melting at 76–77°. Its alcoholic solution becomes an intense red upon the addition of ferric chloride (*Berichte*, 20, 591). This ester is also called *ketipic ester* and results in the action of zinc upon a mixture of oxalic ester and chloracetic ester (*Berichte*, 20, 202).

CARBAMIDES OF THE DICARBOXYLIC ACIDS.

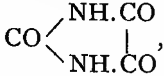
The urea derivatives or carbamides (ureïdes) of these acids are perfectly analogous to those of the dihydric acids (p. 399). By the replacement of two hydrogen atoms in urea we obtain the true ureïdes. The alkalies convert these then into acids of the uric acid group:—



$$CO\begin{array}{l} \diagup NH.CO \\ \qquad\quad | \\ \diagdown NH.CO \end{array} + H_2O = CO\begin{array}{l} \diagup NH.CO.CO.OH \\ \\ \diagdown NH_2 \end{array}.$$

Oxalyl Urea. Oxaluric Acid.

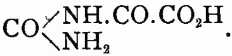
The latter decompose further into urea (also CO_2 and NH_3) and acid, whereas the ureïdes of the divalent acids yield amido-acids. Most of the carbamides were first obtained as decomposition products of uric acid.

Oxalyl Urea, $C_3H_2N_2O_3$ =  $$CO\left\langle\begin{array}{l}NH.CO\\ \quad\;\; |\\ NH.CO\end{array}\right.$$, **Parabanic Acid**, is produced in the energetic oxidation of uric acid and alloxan (p. 443), and is obtained by evaporating a solution of uric acid in three parts of ordinary nitric acid (*Annalen*, 172, 74). It is synthetically prepared by the action of $POCl_3$ upon a mixture of urea and oxalic acid. It is soluble in water and alcohol, but not in ether, and crystallizes in needles or prisms. Under peculiar conditions it crystallizes with one molecule of water, which it does not lose until heated to 150°. Oxalyl urea reacts acid, possesses an acid character, as it contains two imide groups (p. 412) linked to carbonyls, and is ordinarily termed parabanic acid.

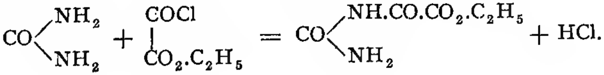
Its *salts* are unstable; water converts them at once into oxalurates. The primary *alkali* salts, *e. g.*, $C_3HKN_2O_3$, are obtained as crystalline precipitates by the addition of potassium or sodium ethylate to an alcoholic solution of parabanic acid. Silver nitrate precipitates the crystalline *disilver salt*, $C_3Ag_2N_2O_3$, from solutions of the acid.

Methyl Parabanic Acid, $C_3H(CH_3)N_2O_3$, is formed by boiling methyl uric acid, or methyl alloxan, with nitric acid, or by treating theobromine with a chromic acid mixture. It is soluble in ether and crystallizes in prisms, which melt at 149.5°. Alkalies convert it into methyl urea and oxalic acid.

Dimethyl Parabanic Acid, $C_3(CH_3)_2N_2O_3$, **Cholestrophane**, is obtained from theïne by boiling with nitric acid, chlorine water or chromic acid, or by heating methyl iodide with silver parabanate, $C_3Ag_2N_2O_3$. It crystallizes in pearly laminæ, melts at 145°, and distils at 276°. Alkalies decompose it into oxalic acid and dimethyl urea; the latter even yields CO_2 and two molecules of $CH_3.NH_2$.

Oxaluric Acid, $C_3H_4N_2O_4$ =  $$CO\left\langle\begin{array}{l}NH.CO.CO_2H\\ NH_2\end{array}\right.$$. Its salts are formed by the action of bases on parabanic acid. They are not readily soluble in water, and usually separate in crystalline form. The *ammonium salt*, $C_3H_3(NH_4)N_2O_4$, and the *silver salt*, $C_3H_3AgN_2O_4$, crystallize in glistening needles. Free oxaluric acid is liberated by mineral acids from its salts as a crystalline powder, dissolving with difficulty. When boiled with alkalies or water it decomposes into urea and oxalic acid; heated to 200° with $POCl_3$ it is again changed into parabanic acid.

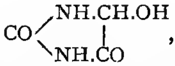
The *ethyl ester*, $C_3H_3(C_2H_5)N_2O_4$, is formed by the action of ethyl iodide on the silver salt, and has been synthetically prepared by letting ethyl oxalyl chloride act upon urea:—



$$CO\left\langle\begin{array}{l}NH_2\\ NH_2\end{array}\right. + \begin{array}{l}COCl\\ |\\ CO_2.C_2H_5\end{array} = CO\left\langle\begin{array}{l}NH.CO.CO_2.C_2H_5\\ NH_2\end{array}\right. + HCl.$$

It crystallizes from warm water in thin, shining needles, which melt with decomposition at 177°. Ammonia and silver nitrate added to the solution of the ether precipitate silver parabanate.

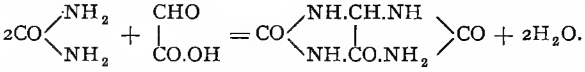
Oxaluramide, $C_3H_5N_3O_3 = CO\begin{cases}NH.CO.CO.NH_2\\NH_2\end{cases}$, *Oxalan*, is produced on heating ethyl oxalurate with ammonia, and by fusing urea with ethyl oxamate, $CO\begin{cases}NH_2\\CO_2.C_2H_5\end{cases}$. It is a crystalline precipitate, dissolving with difficulty in water, and decomposing when boiled with water into urea, ammonia and oxalic acid.



$$CO\begin{cases}NH.CH.OH\\ \quad\;\; | \\NH.CO\end{cases}$$

Glyoxyl Urea, $C_3H_4N_2O_3 = CO\begin{cases}NH.CH.OH\\NH.CO\end{cases}$, **Allanturic Acid,** is the ureïde of glyoxalic acid, $CH(OH)_2.CO_2H$, and is obtained from allantoïn on warming with baryta water or with PbO_2, and by the oxidation of glycolyl urea (hydantoïn, p. 391). It is a deliquescent, amorphous mass, insoluble in alcohol; it forms salts with one equivalent of base. When the potassium salt is boiled with water it decomposes into urea and glyoxalic acid, which is further transposed into glycollic and oxalic acids (see p. 330).

Allantoïn, $C_4H_6N_4O_3$, is a di-ureïde of glyoxalic acid. It is present in the urine of sucking calves, in the allantoïc liquid of cows, and in human urine after the ingestion of tannic acid. It is produced artificially on heating glyoxalic acid (also mesoxalic acid $CO(CO_2H)_2$) with urea to 100°:—



$$2CO\begin{cases}NH_2\\NH_2\end{cases} + \begin{matrix}CHO\\|\\CO.OH\end{matrix} = CO\begin{cases}NH.CH.NH\\ \qquad |\\NH.CO.NH_2\end{cases}\!\!\!\!\!\rangle CO + 2H_2O.$$

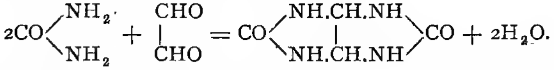
Pyruvil ($C_5H_8N_4O_3$) is formed in a similar manner from urea and pyroracemic acid.

Allantoïn is formed by oxidizing uric acid with PbO_2, MnO_2, potassium ferricyanide, or with alkaline $KMnO_4$ (*Berichte*, 7, 227):—

$$C_5H_4N_4O_3 + O + H_2O = C_4H_6N_4O_3 + CO_2.$$

Allantoïn crystallizes in glistening prisms, which are slightly soluble in cold water, but readily in hot water and in alcohol. It has a neutral reaction, but dissolves in alkalies, forming salts. Ammoniacal silver nitrate precipitates the compound, $C_4H_5AgN_4O_3$—a white powder. When boiled with baryta water it decomposes into CO_2, NH_3, oxalic acid and glycolyl urea (hydantoïn).

Sodium amalgam converts allantoïn into glyco-uril, $C_4H_6N_4O_2$, which is identical with acetylene urea (*Berichte*, 19, 2479):—

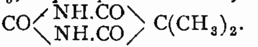
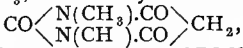


$$2CO\begin{cases}NH_2\\NH_2\end{cases} + \begin{matrix}CHO\\|\\CHO\end{matrix} = CO\begin{cases}NH.CH.NH\\ \qquad |\\NH.CH.NH\end{cases}\!\!\!\!\!\rangle CO + 2H_2O.$$

It crystallizes in long needles or prisms. It breaks down into hydantoïc acid (p. 392) and urea when boiled with baryta water.

Malonyl Urea, $C_4H_4N_2O_3$ =  $CO\left\langle\begin{matrix}NH.CO\\NH.CO\end{matrix}\right\rangle CH_2$, **Barbituric Acid,** the ureïde of malonic acid, is obtained from alloxantin (p. 444) by heating it with concentrated sulphuric acid, and from dibrombarbituric acid by the action of sodium amalgam. It may also be synthetically obtained by heating malonic acid and urea to 100° with $POCl_3$. It crystallizes with two molecules of water in large prisms from a hot solution, and when boiled with alkalies is decomposed into malonic acid and urea.

The hydrogen of CH_2 in malonyl urea can be readily replaced by bromine, NO_2 and the isonitroso-group. The metals in its salts are joined to carbon and may be replaced by alkyls (*Berichte*, 14, 1643; 15, 2846).

When silver nitrate is added to an ammoniacal solution of barbituric acid, a white silver salt, $C_4H_2Ag_2N_2O_3$, is precipitated. Methyl iodide converts this into **Dimethylbarbituric Acid,**  $CO\left\langle\begin{matrix}NH.CO\\NH.CO\end{matrix}\right\rangle C(CH_3)_2$. This forms shining laminæ, does not melt at 200°, and sublimes readily. Boiling alkalies decompose it into CO_2, NH_3, and dimethyl malonic acid. Its isomeride, **β-Dimethyl Barbituric Acid,**  $CO\left\langle\begin{matrix}N(CH_3).CO\\N(CH\ ).CO\end{matrix}\right\rangle CH_2$, is produced from malonic acid and dimethyl urea through the agency of $POCl_3$. It melts at 123°.

Bromine converts barbituric acid, nitro-, isonitroso-, and amido-barbituric acids into **Dibrombarbituric Acid,** $C_4H_2Br_2N_2O_3$ =  $CO\left\langle\begin{matrix}NH.CO\\NH.CO\end{matrix}\right\rangle CBr_2$. This dissolves readily in hot water, in alcohol and in ether. It crystallizes in laminæ or prisms. Boiling water converts it into mesoxalyl-urea (alloxan). Nascent hydrogen or hydriodic acid causes it to revert to barbituric acid, and hydrogen sulphide transforms it into tartronyl-urea (dialuric acid).

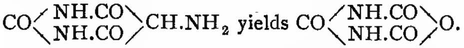
Nitrobarbituric Acid, $C_4H_3(NO_2)N_2O_3$, **Dilituric Acid,** is obtained by the action of fuming nitric acid upon barbituric acid and by the oxidation of violuric acid (*Berichte*, 16, 1135). It crystallizes with three molecules of water in colorless laminæ or prisms, which impart a yellow color to water. It can exchange 3 hydrogen atoms for metals. Its salts are principally those having but one equivalent of metal. They are very stable and, as a general thing, are not decomposed by mineral acids.

Isonitroso-barbituric Acid, $C_4H_2(N.OH)N_2O_3$, **Violuric Acid,** is obtained by acting with potassium nitrite upon barbituric acid. Barium chloride precipitates a red colored salt from the solution; this is decomposed by sulphuric acid. Furthermore, it is prepared (according to the usual methods of forming isonitroso-compounds, p. 214) by the action of hydroxylamine upon alloxan. It crystallizes in yellow, rhombic octahedra with 1 molecule of water. It gives blue, violet and yellow colored salts with one equivalent of metal. The *potassium salt*, $C_4H_2K(NO)N_2O_3 + 2H_2O$, crystallizes in dark blue prisms and dissolves in water with a violet color. Ferric acetate imparts a dark blue color to the solution. When heated with alkalies violuric acid breaks up into urea and isonitroso malonic acid (p. 409).

Amido-barbituric Acid, $C_4H_3(NH_2)N_2O_3$ (Uramil, Dialuramide, Murexan), is obtained in the reduction of nitro- and isonitroso-barbituric acid with hydriodic acid; by boiling thionuric acid with water, and by boiling alloxantin with an ammonium chloride solution:—

$$\underset{\text{Alloxantin.}}{C_8H_4N_4O_7} + NH_3.HCl = \underset{\text{Uramil.}}{C_4H_3(NH_2)N_2O_3} + \underset{\text{Alloxan.}}{C_4H_2N_2O_4} + HCl.$$

Alloxan remains in solution, while uramil crystallizes out. It is only slightly soluble in water, and crystallizes in colorless, shining needles, which redden on exposure. Murexide (p. 445) is produced when the solution is boiled with ammonia. Nitrous acid converts uramil into alloxan:—

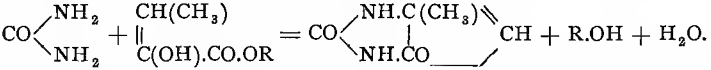


$$\mathrm{CO}\left\langle\begin{matrix}\mathrm{NH.CO}\\ \mathrm{NH.CO}\end{matrix}\right\rangle\mathrm{CH.NH_2}\ \text{yields}\ \mathrm{CO}\left\langle\begin{matrix}\mathrm{NH.CO}\\ \mathrm{NH.CO}\end{matrix}\right\rangle\mathrm{O}.$$

Thionuric Acid, $C_4H_5N_3SO_6 = \mathrm{CO}\left\langle\begin{matrix}\mathrm{NH.CO}\\ \mathrm{NH.CO}\end{matrix}\right\rangle\mathrm{C}\left\langle\begin{matrix}\mathrm{NH_2}\\ \mathrm{SO_3H}\end{matrix}\right.$, sulphamidobarbituric acid, is obtained by heating isonitrosobarbituric acid or alloxan with ammonium sulphite. Its *ammonium salt*, $C_4H_4(NH_4)N_3SO_6 + H_2O$, is made by boiling alloxan with sulphurous acid and ammonia. It forms bright scales. Free thionuric acid is obtained by acting on the lead salt with hydrogen sulphide. It is a readily soluble crystalline mass. It reduces ammoniacal silver solutions, and when boiled with water breaks up into sulphuric acid and uramil.

Uracyl, $C_4H_4N_2O_2 = \mathrm{CO}\left\langle\begin{matrix}\mathrm{NH.CH}\\ \mathrm{NH.CO}\end{matrix}\right\rangle\mathrm{CH}$, the ureïde of β-oxyacrylic acid, CH(OH):CH CO_2H, is only known in its derivatives.

Methyl Uracyl, $C_4H_3(CH_3)N_2O_2 = \mathrm{CO}\left\langle\begin{matrix}\mathrm{NH.C(CH_3)}\\ \mathrm{NH.CO}\end{matrix}\right\rangle\mathrm{CH}$. This is produced when urea acts upon aceto-acetic ester, which reacts in the tautomeric form of β-oxycrotonic ester (*Annalen*, 229, 1):—



$$\mathrm{CO}\left\langle\begin{matrix}\mathrm{NH_2}\\ \mathrm{NH_2}\end{matrix}\right. + \begin{matrix}\mathrm{CH(CH_3)}\\ \Vert\\ \mathrm{C(OH).CO.OR}\end{matrix} = \mathrm{CO}\left\langle\begin{matrix}\mathrm{NH.C(CH_3)}\\ |\\ \mathrm{NH.CO}\end{matrix}\right\rangle\mathrm{CH} + R.OH + H_2O.$$

Concentrated nitric acid converts it into **Nitrouracyl-carboxylic Acid**, $\mathrm{CO}\left\langle\begin{matrix}\mathrm{NH.C(CO_2H)}\\ \mathrm{NH.CO}\end{matrix}\right\rangle\mathrm{C.NO_2}$. This passes, by elimination of CO_2H, and reduction of its nitro-group, into *amidouracyl*, $\mathrm{CO}\left\langle\begin{matrix}\mathrm{NH.CH}\\ \mathrm{NH.CO}\end{matrix}\right\rangle\mathrm{C.NH_2}$, and *oxyuracyl*, $\mathrm{CO}\left\langle\begin{matrix}\mathrm{NH.CH}\\ \mathrm{NH.CO}\end{matrix}\right\rangle\mathrm{C.OH}$, *isobarbituric acid*. Bromine water converts the latter into *isodialuric acid*, $\mathrm{CO}\left\langle\begin{matrix}\mathrm{NH.C(OH)}\\ \mathrm{NH.CO}\end{matrix}\right\rangle\mathrm{C.OH}$. This yields uric acid when heated with urea and sulphuric acid (p. 445) (*Berichte*, 21, 999; *Annalen*, 251, 235).

Tartronyl Urea, $C_4H_4N_2O_4 = \mathrm{CO}\left\langle\begin{matrix}\mathrm{NH.CO}\\ \mathrm{NH.CO}\end{matrix}\right\rangle\mathrm{CH.OH}$, dialuric acid, the ureïde of tartronic acid, $CH(OH)(CO_2H)_2$, is formed by the reduction of mesoxalyl urea (alloxan) with zinc and hydrochloric acid, and from dibrombarbituric acid by the action of hydrogen sulphide. On adding hydrocyanic acid and potassium carbonate to an aqueous solution of alloxan, potassium dialurate separates but potassium oxalurate remains dissolved :—

$$2C_4H_2N_2O_4 + 2KOH = \underset{\text{Potassium Dialurate.}}{C_4H_3KN_2O_4} + \underset{\text{Potassium Oxalurate.}}{C_3H_3KN_2O_4} + CO_2.$$

Dialuric acid crystallizes in needles or prisms, has a very acid reaction and forms salts with 1 and 2 equivalents of the metals. It becomes red in color in the air, absorbs oxygen and passes over into alloxantin, $2C_4H_4N_2O_4 + O = C_8H_4N_4O_7 + 2H_2O$.

Mesoxalyl Urea, $C_4H_2N_2O_4 = CO\left\langle\begin{matrix}NH.CO\\NH.CO\end{matrix}\right\rangle CO$, **Alloxan,** the ureïde of mesoxalic acid, is produced by the careful oxidation of uric acid, or alloxantin with nitric acid or chlorine and bromine.

Preparation.—Add uric acid gradually to cold nitric acid of specific gravity 1.4, as long as a reaction occurs. Then let the whole stand for some time. The separated, crystalline mass of alloxan is drained upon an asbestos filter, warmed upon a water bath to expel all nitric acid, and then recrystallized from water; alloxantin remains in the mother-liquor.

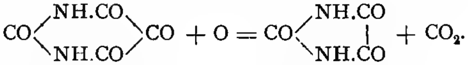
Moisten alloxantin with concentrated nitric acid (sp. gr. 1.46), let stand until it has been completely changed to alloxan (a small portion should dissolve readily in cold water), and then purify the latter as already described.

Alloxan crystallizes from warm water in long, shining, rhombic prisms, with 4 molecules of H_2O. When exposed to the air they effloresce with separation of $3H_2O$. The last molecule of water is intimately combined (p. 434), as in mesoxalic acid, and does not escape until heated to 150°. Small stable crystals, with 1 H_2O separate out from hot solutions. Alloxan is easily soluble in water, has a very acid reaction and possesses a disagreeable taste. The solution placed on the skin slowly stains it a purple red. Ferrous salts impart a deep indigo blue color to the solution. When hydrocyanic acid and ammonia are added to the aqueous solution the alloxan decomposes into CO_2, dialuric acid and oxaluramide (p. 440), which separates as a white precipitate (reaction for detection of alloxan).

The primary alkali sulphites unite with alloxan just as they do with mesoxalic acid, and we can obtain crystalline compounds, *e.g.*, $C_4H_2N_2O_4.SO_3KH + H_2O$. Pure alloxan can be preserved without undergoing decomposition, but in the presence of even minute quantities of nitric acid it is converted into alloxantin. Alkalies, lime or baryta water, change it to alloxanic acid, even when acting in the cold. Its aqueous solution undergoes a gradual decomposition (more rapid on heating) into alloxantin, parabanic acid and CO_2:—

$$3C_4H_2N_2O_4 = \underset{\text{Alloxantin.}}{C_8H_4N_4O_7} + \underset{\text{Oxalyl Urea.}}{C_3H_2N_2O_3} + CO_2.$$

Boiling dilute nitric acid oxidizes alloxan to parabanic acid (oxalyl urea) and CO_2:—



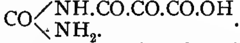
Mesoxalyl Urea. Oxalyl Urea.

The mesoxalic acid residue, like the free acid (p. 434), splits off a CO-group, readily forming oxalyl.

Reducing agents, like hydriodic acid, change alloxan, in the cold, to alloxantin, on warming, however, into tartronyl urea (dialuric acid).

Methyl Alloxan, $C_4H(CH_3)N_2O_4$, is produced by the oxidation of methyl uric acid. Alkalies convert it at once into methyl alloxanic acid. Nitric acid changes it to methyl parabanic acid (p. 439).

Dimethyl Alloxan, $CO(N.CH_3)_2C_3O_3$, is produced when aqueous chlorine (hydrochloric acid and $KClO_3$) acts on theïne, and by the careful oxidation of tetramethyl alloxantin with nitric acid. When the solution is concentrated, dimethyl alloxan remains as a non-crystallizable syrup. It gives all the reactions of alloxan. H_2S reduces it to tetramethyl alloxantin (see below). By energetic oxidation, it yields dimethyl oxalyl urea (p. 405).

Alloxanic Acid, $C_4H_4N_2O_5$ =  $CO\begin{cases}NH.CO.CO.CO.OH\\NH_2\end{cases}$. When the alkalies act on alloxan the latter absorbs water and passes into the acid. If baryta water be added to a warm solution of alloxan, as long as the precipitate which forms continues to dissolve, barium alloxanate, $C_4H_2BaN_2O_5 + 4H_2O$, will separate out in needles when the solution cools. To obtain the free acid, decompose the barium salt with sulphuric acid and evaporate at a temperature of 30–40°. A mass of crystals is obtained by this means. Water dissolves them easily. Alloxanic acid shows a very acid reaction, dissolves zinc, and is indeed a dibasic acid, inasmuch as both the hydrogen of carboxyl and of the imide group can be exchanged for metals. When the salts are boiled with water, they decompose into urea and mesoxalates.

By the union of two molecules of the ureïdes of the dicarboxylic acids we get the compounds oxalantin, alloxantin, and hydurilic and purpuric acids. These are termed di-ureïdes.

Oxalantin, $C_8H_8N_4O_6$, **Leucoturic Acid,** is obtained by the action of zinc and hydrochloric acid upon oxalyl urea:—$2C_3H_2N_2O_8 + H_2 = C_6H_6N_4O_6$. H_2S separates it from the zinc salt. It forms crystalline crusts which dissolve with difficulty in water, and it also reduces ammoniacal solutions of both silver and mercury.

Alloxantin, $C_8H_4N_4O_7$, is obtained by reducing alloxan with $SnCl_2$, zinc and hydrochloric acid, or H_2S in the cold: $2C_4H_2N_2O_4 + H_2 = C_8H_4N_4O_7 + H_2O$; or by mixing solutions of alloxan and dialuric acid: $C_4H_2N_2O_4 + C_4H_4N_2O_4 = C_8H_4N_4O_7 + H_2O$. Most readily prepared by warming uric acid with dilute nitric acid (*Annalen*, 147, 367). It crystallizes from hot H_2O in small, hard prisms with $3H_2O$ and turns red in air containing ammonia. Its solution has an acid reaction; ferric chloride and ammonia give it a deep blue color, and baryta water produces a violet precipitate, which on boiling is converted into a mixture of barium alloxanate and dialurate.

Tetramethyl Alloxantin, $C_8(CH_3)_4N_4O_7 = C_{12}H_{12}N_4O_7$, **Amalic Acid,** is formed by the action of nitric acid or chlorine water upon theïne, or better, by the reduction of dimethyl alloxan (see above) with hydrogen sulphide (*Annalen*, 215, 258):—

$$2C_4(CH_3)_2N_2O_4 + H_2 = C_6(CH_3)_4N_4O_7 + H_2O.$$

It consists of colorless, sparingly soluble crystals, which impart a red color to the skin; alkalies and baryta water give it a violet-blue color. When carefully oxidized by nitric acid, or by the action of chlorine (*Annalen*, 221, 339) it is again altered to dimethyl alloxan; more energetic reaction produces dimethyl parabanic acid.

Hydurilic Acid, $C_8H_6N_4O_6$. The ammonium salt is formed on boiling alloxantin with dilute sulphuric acid; by heating dialuric acid with glycerol to 150°; and also on heating aqueous alloxan or alloxantin to 170°. The free acid is obtained by decomposing the copper salt with hydrochloric acid. It crystallizes from hot water in little prisms having $2H_2O$, and is a dibasic acid. Ferric chloride imparts a dark green color to the solution of the acid or its salts. Ordinary nitric acid decomposes hydurilic acid into nitro- and nitroso-barbituric acid; fuming nitric acid forms alloxan.

Purpuric Acid, $C_8H_5N_5O_6$, is not known in the free state, because as soon as it is liberated from its salts by mineral acids it immediately decomposes into alloxan and uramil. The ammonium salt, $C_8H_4(NH_4)N_5O_6 + H_2O$, is the dye-stuff *murexide*. This is formed by heating alloxantin to 100° in ammonia gas; by mixing ammoniacal solutions of alloxan and uramil:—

$$C_4H_2N_2O_4 + C_4H_5N_3O_3 + NH_3 = C_8H_4(NH_4)N_5O_6 + H_2O;$$

and by evaporating uric acid with dilute nitric acid and pouring ammonia over the residue (murexide reaction). It is most readily obtained from uramil (p. 441). Dissolve 4 parts of the latter in dilute ammonium hydroxide, add 3 parts of mercuric oxide and heat to boiling, when mercury will separate and the solution assume a dark-red color:—

$$2C_4H_5N_3O_3 + O = C_8H_4(NH_4)N_5O_6 + H_2O.$$

Murexide separates from the solution on cooling. It forms four-sided plates or prisms with one molecule of H_2O, and has a gold-green color. It dissolves in water with a purple-red color, but is insoluble in alcohol and ether. It dissolves with a dark blue color in potash; on boiling NH_3 is disengaged and the solution decolorized.

Uric Acid, $C_5H_4N_4O_3$, occurs in the juice of the muscles, in the blood and in the urine, especially of the carnivoræ, the herbivoræ separating hippuric acid; also, in the excrements of birds, reptiles and insects. When urine is exposed for awhile to the air, uric acid separates; this also occurs in the organism (formation of gravel and joint concretions) in certain abnormal conditions.

Uric acid is prepared artificially by heating glycocoll with urea (10 parts) to 200–230° (*Berichte*, 17, 443,), or trichlorlactamide with urea (*Berichte*, 20, Ref. 472). It may be directly synthesized by heating isodialuric acid (p. 442) and urea with sulphuric acid (p. 446) (Behrend, *Berichte*, 22, Ref. 397).

Uric acid is best prepared from guano and the excrements of reptiles. Guano is boiled with a hot borax solution (1 part borax in 120 parts H_2O) and the uric acid precipitated from the filtrate by hydrochloric acid. Or, after removing the phosphates from guano by means of dilute hydrochloric acid, it is dissolved in concentrated sulphuric acid (in equal weight), and the uric acid precipitated by pouring the solution into water (12–15 vols). To obtain the acid pure, it is dissolved in caustic potash and carbon dioxide conducted into the liquid, when potassium urate will be precipitated; hydrochloric acid sets free the uric acid.

The excrements of reptiles (ammonium urate) are boiled with dilute potassium or sodium hydroxide until the odor of ammonia is no longer perceptible, the hot solution filtered and the filtrate poured into dilute hydrochloric acid.

Uric acid is precipitated as a shining, white powder, from solutions of its salts. It is odorless and tasteless, insoluble in alcohol and ether, and dissolves with difficulty in water; 1 part requires 15,000 parts water of 20° for its solution, and 1800 parts at 100°. Its solubility is increased by the presence of salts like sodium phosphate and borate. Water precipitates it from its solution in concentrated sulphuric acid. On evaporating uric acid to dryness with nitric acid, we obtain a yellow residue, which assumes a purple-red color if moistened with ammonia, or violet with caustic potash or soda (murexide reaction, p. 445). Heat decomposes uric acid into NH_3, CO_2, urea and cyanuric acid.

Uric acid acts like a weak dibasic acid, forming chiefly, however, salts containing but one equivalent of metal. The secondary alkali salts are obtained by dissolving the primary salts or the free acid in the hydroxides of potassium and sodium; they show a very alkaline reaction, and are changed to the primary form by CO_2 and water. When CO_2 is conducted through the alkaline solution, the primary salts are precipitated. Uric acid forms primary salts with the alkaline carbonates.

The *dipotassium salt*, $C_5H_2K_2N_4O_3$, separates in needles when its solution is evaporated. It dissolves easily in potash and in 40 parts of water at ordinary temperatures. The *primary salt*, $C_5H_3KN_4O_3$, is precipitated from solutions of the dipotassium salt as a jelly, which soon becomes granular and dissolves in 800 parts of water at 20°. The *primary sodium salt* is more insoluble. The *primary ammonium salt*, $C_5H_3(NH_4)N_4O_3$, is precipitated as a sparingly soluble powder, by ammonium chloride, from the solutions of the other salts.

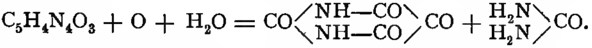
Methyl Uric Acid, $C_5H_3(CH_3)N_4O_3$, is obtained by heating primary lead urate with methyl iodide and ether to 160°. It consists of small needles, which are rather insoluble in water. When heated with concentrated hydrochloric acid to 170° it decomposes into NH_3, CO_2, methylamine and glycocoll (*Berichte*, 17, 330).

Dimethyl Uric Acid, $C_5H_2(CH_3)_2N_4O_3$, obtained from the secondary lead salt, crystallizes with one molecule of water, which is not expelled until heated to 160°. It yields the same decomposition products as the preceding (2 molecules methylamine). Both acids are capable of forming primary and secondary salts, which are perfectly analogous to those of uric acid.

Careful oxidation converts dimethyl uric acid (analogous to uric acid) into methyl alloxan and methyl urea.

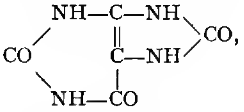
Consult *Berichte*, 17, 1777, for an isomeric β-methyl- and β-dimethyl uric acid.

When uric acid is carefully oxidized, either with cold nitric acid or with potassium chlorate and hydrochloric acid, it yields mesoxalyl urea and urea:—

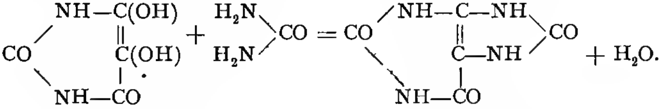


$$C_5H_4N_4O_3 + O + H_2O = CO\left\langle\begin{matrix}NH-CO\\NH-CO\end{matrix}\right\rangle CO + \left.\begin{matrix}H_2N\\H_2N\end{matrix}\right\rangle CO.$$

Its structure is probably represented by the formula:—



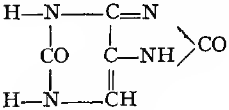
which was first proposed by Medicus. This would make it the diureïde of acrylic acid, or more correctly, that of the hypothetical compound, $CO = C(OH)-CO_2H$ (*Berichte*, 17, 1776). This is demonstrated by its synthesis from urea and the amide of trichlorlactic acid (p. 445), and more directly by its synthesis from isodialuric acid and urea:—



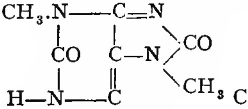
Isodialuric Acid. Uric Acid.

The presence of four imide groups explains how it and also dimethyl uric acid are capable of forming salt-like compounds with 1 and 2 equivalents of the metals.

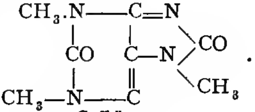
Guanine, xanthine, hypoxanthine, and carnine stand in close relation to uric acid. Like it they occur as products of the metabolism of the animal organism. Xanthine and hypoxanthine occur in the extract of tea. Theobromine and caffeïne found in the vegetable kingdom are very similar to them; these are also included among the alkaloids because of their basic character. An approximate representation of the constitution of xanthine, theobromine and caffeïne is given in the following formulas:—



Xanthine.

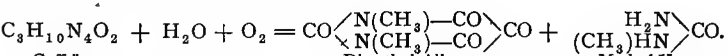


Theobromine.



Caffeïne.

They would accordingly be the di-ureïdes of an acid with three carbon atoms (as mesoxalic acid). Theobromine is dimethyl- and caffeïne trimethyl-xanthine. They may be artificially prepared by introducing methyl into xanthine. The decomposition of caffeïne (by action of chlorine) into dimethyl oxalyl-urea (dimethyl alloxan, p. 444) and methyl urea (also *Annalen*, 221, 313) is especially suggestive in explaining the constitution:—



$$C_8H_{10}N_4O_2 + H_2O + O_2 = CO\left\langle\begin{matrix}N(CH_3)\text{—}CO\\N(CH_3)\text{—}CO\end{matrix}\right\rangle CO + \left.\begin{matrix}H_2N\\(CH_3)HN\end{matrix}\right\rangle CO.$$

Caffeïne. Dimethyl Alloxan. Methyl Urea.

Nitrous acid converts guanine into xanthine, and in its decomposition yields guanidine, $\left.\begin{matrix}H_2N\\H_2N\end{matrix}\right\rangle C = NH$; hence we can consider it as xanthine, in which a guanidine residue occurs instead of that of urea, *i. e.*, the oxygen of a CO-group has been replaced by imide, NH.

Sodium amalgam converts uric acid into xanthine and sarcine, hence all these compounds are intimately related to uric acid, which fact is manifest in their analogous formulas.

Guanine, $C_5H_5N_5O$, occurs in the pancreas of some animals and very abundantly in guano.

To obtain it, guano is boiled several times with milk of lime until the liquid no longer shows a brown color; in this manner coloring substances and certain acids are removed; uric acid and guanine constitute the chief portion of the residue. The latter is boiled with soda, filtered, sodium acetate added, and the whole strongly acidulated with hydrochloric acid, which causes the precipitation of guanine, accompanied by some uric acid. The precipitate is dissolved in boiling hydrochloric acid and the guanine thrown down by ammonium hydroxide.

Guanine is an amorphous powder, insoluble in water, alcohol and ether. It yields crystalline salts with 1 and 2 equivalents of acid, *e. g.*, $C_5H_5N_5O.2HCl$. It also forms crystalline compounds with bases. Silver nitrate gives a crystalline precipitate, $C_5H_5N_5O.NO_3Ag$.

Nitrous acid converts guanine into xanthine. Potassium chlorate and hydrochloric acid decompose it into parabanic acid, guanidine and CO_2 (see above).

Xanthine, $C_5H_4N_4O_2$, occurs in slight amounts in many animal secretions, in the blood, in urine, in the liver, in some forms of calculi and in tea extract. It results from the action of nitrous acid upon guanine (*Annalen*, 215, 309). It is a white, amorphous mass, somewhat soluble in boiling water, and combines with both acids and bases. It is readily soluble in boiling ammonia; silver nitrate precipitates $C_5H_2Ag_2N_4O_2 + H_2O$ from its solution. The corresponding lead compound yields theobromine (dimethyl xanthine) when heated to 100° with methyl iodide. When xanthine (analogous to caffeïne, page 449) is warmed with potassium chlorate and hydrochloric acid it splits into alloxan and urea.

Sarcine, $C_5H_4N_4O$, Hypoxanthine, is a constant attendant of xanthine in the animal organism, and is distinguished principally by the difficult solubility of its hydrochloride. It consists of needles not very soluble in water, but dissolved by alkalies and acids. Silver nitrate precipitates the compound $C_5H_2Ag_2N_4O + H_2O$ from ammoniacal solutions.

Adenine, $C_5H_5N_5$, has been isolated from beef pancreas. It also occurs in tea extract. It crystallizes in leaflets with pearly lustre. It has three molecules of water of crystallization. At 54° the salt becomes white in color, owing to loss of water. Nitrous acid converts it into hypoxanthine. It is, therefore, an amide, $C_5H_3(NH_2)N_4$, or imide, $C_5H_4(NH)N_4$, (*Berichte*, 23, 225).

Carnine, $C_7H_8N_4O + H_2O$, has been found in the extract of beef. It is a powder, rather easily soluble in water, and forms a crystalline compound with hydrochloric acid. Bromine water or nitric acid converts carnine into sarcine.

Theobromine, $C_7H_8N_4O_2 = C_5H_2(CH_3)_2N_4O_2$, dimethyl xanthine, occurs in cocoa-beans (from *Theobroma Cacao*) and is prepared by introducing methyl into xanthine (see above).

Divided cocoa-beans are boiled with water, tannic acid and other substances precipitated by basic lead acetate, and hydrogen sulphide conducted into the filtrate to remove excess of lead. The solution is then evaporated to dryness and the theobromine extracted from the residue with alcohol.

Theobromine is a crystalline powder with a bitter taste and dissolves with difficulty in hot water and alcohol, but rather easily in ammonium hydroxide. It sublimes (about 290°) without decomposition, when it is carefully heated. It has a neutral reaction, but yields crystalline salts on dissolving in acids; much water will decompose these. Silver nitrate precipitates the compound, $C_7H_7AgN_4O_2$, in crystalline form from the ammoniacal solution after protracted heating. When this salt is heated with methyl iodide it yields methyl theobromine, $C_7H_7(CH_3)N_4O_2$, *i. e.*, caffeïne.

Theophylline, $C_7H_8N_4O_2 = C_5H_2(CH_3)_2N_4O_2$, is isomeric with theobromine. It is present in tea extract. It contains one molecule of water of crystallization, which it loses at 110°. The introduction of methyl converts it into theïne. (*Berichte*, 21, 2164).

Caffeïne, Theïne, $C_8H_{10}N_4O_2$, methyl theobromine, trimethyl xanthine (p. 447), occurs in the leaves and beans of the coffee tree (½ per cent.), in tea (2–4 per cent.), in Paraguay tea (from *Ilex paraguayensis*), and in guarana (about 5 per cent.) the roasted pulp of the fruit of *Paullinia sorbilis*. The caffeïne is procured from these sources, just as theobromine is obtained. It is also found in minute quantities in cocoa.

Caffeïne consists of long, silky needles with 1 molecule of water; they are only slightly soluble in cold water, and alcohol. At 100° it loses its water, melts at 225° and sublimes at higher temperatures.

It has a feeble bitter taste and forms salts with the strong mineral acids; water readily decomposes them. On evaporating a solution of chlorine water containing traces of caffeïne we get a reddish-brown spot, which acquires a beautiful violet-red color when dissolved in ammonia water.

Sodium hydroxide converts theïne into *caffeïdine carboxylic acid*, $C_7H_{11}N_4O.CO_2H$, which readily decomposes into CO_2 and *caffeïdine*, $C_7H_{12}N_4O$ (*Berichte*, **16**, 2309). The latter is also obtained when caffeïne is boiled with baryta water; it is a readily soluble, strong base and decomposes on protracted boiling into NH_3, methylamine, formic acid and methyl glycocoll. For other caffeïne derivatives (apocaffeïne, caffuric acid, caffolin) see *Annalen*, **215**, 261, and **228**, 141.

Chlorine water breaks caffeïne up into dimethyl alloxan and methylurea (p. 448). By energetic action of chlorine, dimethyl parabanic acid is produced. This is also formed in the oxidation of theïne with chromic acid, while theobromine yields methyl parabanic acid.

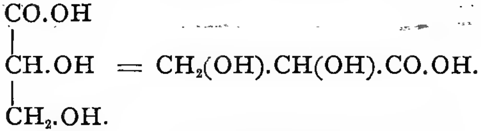
TRIVALENT (TRIHYDRIC) COMPOUNDS.

The trivalent compounds are derived from the hydrocarbons in the same manner as the mono- and divalent; three hydrogen atoms are replaced by three monovalent groups. Their methods of formation and transposition are also perfectly analogous to those of the mono- and di-derivatives.

When three hydroxyl groups are introduced **trivalent (trihydric) alcohols** are formed:—

$$C_3H_5(OH)_3 = \underset{\text{Glycerol.}}{CH_2(OH).CH(OH).CH_2.OH.}$$

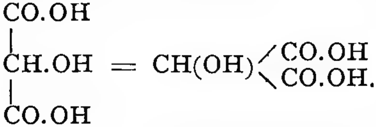
By the conversion of one primary alcoholic group, $CH_2.OH$, into carboxyl, we obtain the *trivalent monobasic acids*, in which two alcoholic hydroxyls remain, hence they can be termed dioxy-monocarboxylic acids:—



$$\begin{array}{l} CO.OH \\ | \\ CH.OH \\ | \\ CH_2.OH. \end{array} = CH_2(OH).CH(OH).CO.OH.$$

Trivalent Monobasic Acid,
Glyceric Acid or Dioxypropionic Acid.

The *trivalent dibasic acids* contain two carboxyl groups and one alcohol group; hence may be called oxy-dicarboxylic acids:—



$$\begin{array}{l} CO.OH \\ | \\ CH.OH \\ | \\ CO.OH \end{array} = CH(OH)\left\langle \begin{array}{l} CO.OH \\ CO.OH. \end{array} \right.$$

Trivalent Dibasic Acid,
Tartronic or Oxymalonic Acid.

The *tribasic acids*, finally, contain three carboxyl groups:—

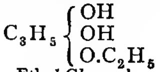
$$C_3H_5(CO_2H)_3.$$

Tribasic or Tricarboxylic Acid.

Many derivatives attach themselves to the trivalent alcohols and acids.

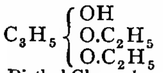
TRIVALENT (TRIHYDRIC) ALCOHOLS.

. In these, three hydrogen atoms can be replaced by alcohol or acid residues, forming ethers and esters:—



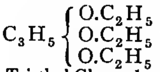
$$C_3H_5\left\{\begin{array}{l}OH\\OH\\O.C_2H_5\end{array}\right.$$

Ethyl Glycerol.



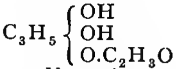
$$C_3H_5\left\{\begin{array}{l}OH\\O.C_2H_5\\O.C_2H_5\end{array}\right.$$

Diethyl Glycerol.



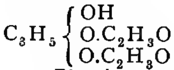
$$C_3H_5\left\{\begin{array}{l}O.C_2H_5\\O.C_2H_5\\O.C_2H_5\end{array}\right.$$

Triethyl Glycerol.



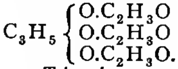
$$C_3H_5\left\{\begin{array}{l}OH\\OH\\O.C_2H_3O\end{array}\right.$$

Monacetin.



$$C_3H_5\left\{\begin{array}{l}OH\\O.C_2H_3O\\O.C_2H_3O\end{array}\right.$$

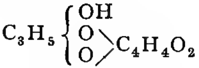
Diacetin.



$$C_3H_5\left\{\begin{array}{l}O.C_2H_3O\\O.C_2H_3O\\O.C_2H_3O.\end{array}\right.$$

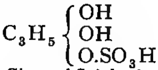
Triacetin.

The polybasic acids yield similar esters:—



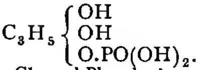
$$C_3H_5\left\{\begin{array}{l}OH\\O\\O\end{array}\right.\!\!>C_4H_4O_2$$

Succinin.



$$C_3H_5\left\{\begin{array}{l}OH\\OH\\O.SO_3H\end{array}\right.$$

Glycerol Sulphuric Acid.



$$C_3H_5\left\{\begin{array}{l}OH\\OH\\O.PO(OH)_2.\end{array}\right.$$

Glycerol Phosphoric Acid.

The esters of the haloid acids, like

$C_3H_5(OH)_2Cl$	$C_3H_5(OH)Cl_2$	$C_3H_5Cl_3$,
Monochlorhydrin.	Dichlorhydrin.	Trichlorhydrin.

may be viewed as substitution products of the di- and trivalent alcohols.

Glycerol, $C_3H_5(OH)_3$, is the first member of the trihydric alcohols. Lower homologues cannot exist, because in general one carbon atom is capable of linking only one hydroxyl group in such a manner that the hydrogen in it will be exchangeable in any further replacement. Ethers and esters of trihydroxyl compounds, with one and two carbon atoms, exist (p. 298).

The trihydroxyl derivatives are formed artificially in the same manner as the mono- and di-hydroxyl compounds (p. 297). They can be obtained by oxidizing the unsaturated alcohols with potassium permanganate (pp. 82, 297). Thus allyl alcohol yields glycerol:—

$$CH_2:CH.CH_2.OH + O + H_2O = CH_2(OH).CH(OH).CH_2(OH).$$

Amyl glycerol, $C_2H_5.CH(OH).CH(OH).CH_2(OH)$, is obtained from ethyl viny carbinol, $C_2H_5.CH(OH).CH:CH_2$, etc. (*Berichte*, 21, Ref. 183; 22, Ref. 798).

Certain hydrates of the fatty acids, having constant boiling points at times (see formic acid), may be considered as trihydroxyl derivatives; hence, they have been called ortho-acids:—

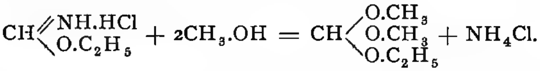
$$\underset{\text{Orthoformic Acid.}}{CH_2O_2 + H_2O = CH(OH)_3} \qquad \underset{\text{Orthoacetic Acid.}}{CH_3.CO_2H + H_2O = CH_3.C(OH)_3,}$$

just as the hydrate of nitric acid, $NO_3H + H_2O = NO(OH)_3$, is termed ortho-nitric acid.

We get the esters of orthoformic acid by heating chloroform with an alcoholic solution of sodium alcoholates:—

$$CHCl_3 + 3CH_3.ONa = CH(O.CH_3)_3 + 3NaCl;$$

or by the union of form-imido-ethers (p. 292) with alcohols, resulting in mixed esters (*Berichte*, 16, 1645):—



$$CH\begin{cases}NH.HCl \\ O.C_2H_5\end{cases} + 2CH_3.OH = CH\begin{cases}O.CH_3 \\ O.CH_3 \\ O.C_2H_5\end{cases} + NH_4Cl.$$

When sodium mercaptides act on chloroform, we obtain esters of orthothioformic acid, *e. g.*, $CH(S.CH_3)_3$.

Methyl Orthoformic Ester, $CH(O.CH_3)_3$, boils at 102°, and has a specific gravity 0.974 at 23°. The **Triethyl Ester** $CH(O.C_2H_5)_3$, is an aromatic smelling liquid, insoluble in water, and boiling at 146°; sp. gr. 0.896. It decomposes into ethyl formic, and ethyl acetic esters, when heated with glacial acetic acid.

The **Triallyl Ester,** $CH(O.C_3H_5)_3$, formed by the action of metallic sodium upon chloroform and allyl alcohol, boils about 200°.

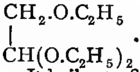
Ethyl Orthoformic Ester, $CH(S.C_2H_5)_3$, from sodium chloroform and sodium mercaptide, is an oil with an odor like that of garlic. When oxidized it becomes a *disulphone*, $CH_2(SO_2.C_2H_5)_2$ (p. 307).

Methine Trisulphonic Acid, $CH(SO_3H)_3$, is obtained by heating chloropicrin, $CCl_3(NO)_2$, with a concentrated aqueous solution of sodium sulphite, or by heating calcium methyl sulphonate (p. 153) with fuming sulphuric acid. This acid, like all sulphonic acids, is very stable and is not affected by boiling alkalies.

Ethyl Ortho-acetic Ester, $CH_3.C(O.C_2H_5)_3$, triethyl acetyl ester, is obtained by heating α-trichlorethane, $CH_3.CCl_3$, with an ethereal solution of sodium ethylate. It boils at 142°, and when heated with water to 120° breaks up into acetic acid and alcohol.

Isomeric with the preceding is

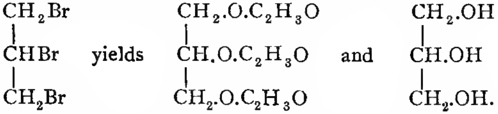
Triethyl Ethenyl Ester,



$$\begin{array}{l}CH_2.O.C_2H_5 \\ | \\ CH(O.C_2H_5)_2\end{array}$$

. which is obtained from chloracetal, $CH_2Cl.CH(O.C_2H_5)_2$ (p. 305). It boils at 186°.

Glycerol, $C_3H_8O_3 = C_3H_5(OH_3)$, glycerine, is produced in small quantities in the alcoholic fermentation of sugar. It is prepared exclusively from the fats and oils, which are glycerol esters of the fatty acids (p. 458). When the fats are saponified by bases or sulphuric acid, they decompose, like all esters, into fatty acids and the alcohol—glycerol. It is obtained synthetically from allyl tribromide (p. 104) by converting the latter, with silver acetate, into glycerol acetate and saponifying this ester with boiling alkalies:—



$$\begin{array}{l} CH_2Br \\ | \\ CHBr \\ | \\ CH_2Br \end{array} \quad \text{yields} \quad \begin{array}{l} CH_2.O.C_2H_3O \\ | \\ CH.O.C_2H_3O \\ | \\ CH_2.O.C_2H_3O \end{array} \quad \text{and} \quad \begin{array}{l} CH_2.OH \\ | \\ CH.OH \\ | \\ CH_2.OH. \end{array}$$

Glycerol is similarly formed from glycerol trichloride (from propylene chloride) by heating it with water to 170°.

In preparing glycerol from fats (chiefly olive oil) the latter were formerly saponified by boiling them with lead oxide and water. The aqueous solution of glycerol was separated from the insoluble lead salt of the fatty acids (lead plaster, p. 216), the dissolved lead precipitated by hydrogen sulphide and the filtrate concentrated by evaporation.

At present glycerol is produced in large quantities in the manufacture of stearic acid; the fats are saponified by means of superheated steam, converting them directly into glycerol and fatty acids. In most stearic acid factories sulphuric acid is employed for the saponification. The glycerol then exists as glycerol-sulphuric acid (p. 454) in the aqueous solution. To liberate the glycerol the solution is boiled with lime, the gypsum filtered off, the liquid concentrated and distilled with superheated steam. In order to obtain a pure product the glycerol is again distilled under diminished pressure.

Anhydrous glycerol is a thick, colorless syrup, of specific gravity 1.265 at 15°. Under certain conditions it solidifies to a white, crystalline mass, which melts at +17°. Under ordinary atmospheric pressure it boils at 290° (cor.) without decomposition; under diminished pressure, or with superheated steam, it distils entirely unaltered. See *Berichte*, 17, Ref. 522, for the specific gravities and boiling points of its aqueous solutions. It has a pure, sweet taste, hence the name glycerol. It absorbs water very energetically when exposed and mixes in every proportion with water and alcohol, but is insoluble in ether. It dissolves the alkalies, alkaline earths and many metallic oxides, forming with them, in all probability, metallic compounds similar to the alcoholates (p. 126).

When glycerol is distilled with dehydrating substances, like sulphuric acid and phosphorus pentoxide, it decomposes into water and acroleïn (p. 199). It sustains a similar and partial decomposition when it is distilled alone. When fused with caustic potash, it evolves hydrogen, and yields acetic and formic acids. Platinum black, or dilute nitric acid, oxidizes it to glyceric and tartronic acids, but under energetic oxidation the products are oxalic acid, glycollic acid, glyoxylic and other acids. Moderated oxidation (with nitric acid, or bromine) produces *glycerose*, which consists chiefly of dioxyacetone, $CO(CH_2.OH)_2$. This unites with CNH and forms trioxybutyric acid (*Berichte*, 22, 106; 23, 387). Phosphorus iodide or hydriodic acid converts it into allyl iodide, isopropyl iodide and propylene (p. 98). In the presence of yeast at 20–30° it ferments, forming propionic acid.

Nitroglycerine, Trinitrin, glycerol nitric ester, $C_3H_5(O.NO_2)_3$ (p. 302), is produced by the action of a mixture of sulphuric and nitric acids upon glycerol. The latter is added, drop by drop, to a well-cooled mixture of equal volumes of concentrated nitric and sulphuric acids, as long as it dissolves; the solution is then poured into water, and the separated, heavy oil (nitroglycerine) is washed with water and dried by means of calcium chloride.

Nitroglycerine is a colorless oil, of sp. gr. 1.6, and becomes crystalline at —20°. It has a sweet taste and is poisonous when taken inwardly. It is insoluble in water, dissolves with difficulty in cold alcohol, but is easily soluble in wood spirit and ether. Heated quickly, or upon percussion, it explodes very violently (*Nobel's explosive oil*); mixed with *kieselguhr* it forms *dynamite.*

Alkalies convert nitroglycerine into glycerol and nitric acid; ammonium sulphide also regenerates glycerol. Both reactions prove that nitroglycerine is not a nitro-compound, but a nitric-acid ester.

Glycerol-Nitrite, $C_3H_5(O.NO)_3$, is formed by the action of N_2O_3 upon glycerol. It boils at 150° with partial decomposition. Water breaks it up with evolution of oxides of nitrogen. Its isomeride, **Trinitropropane,** $C_3H_5(NO_2)_3$, is obtained from glyceryl bromide by the action of silver nitrite. It is an oil, boiling at 200°.

Glycerol-Sulphuric Acid, $C_3H_5\begin{cases}(OH)_2\\O.SO_3H\end{cases}$, is formed by mixing 1 part glycerol with 1 part of sulphuric acid. The free acid decomposes when its aqueous solution is heated. Its salts are readily soluble; the calcium salt is crystalline.

Glycerol-Phosphoric Acid, $C_3H_5\begin{matrix}\diagup(OH)_2\\ \diagdown O.PO_3H_2\end{matrix}$, occurs combined with the fatty acids and choline as lecithin (see this) in the yolk of eggs, in the brain, in the bile, and in the nervous tissue. It is produced on mixing glycerol with metaphosphoric acid. The free acid is a stiff syrup, which decomposes into glycerol and phosphoric acid when it is heated with water. It yields easily soluble salts with two equivalents of metal. The calcium salt is more insoluble in hot than in cold water; on boiling its solution, it is deposited in glistening leaflets.

HALOID ESTERS OF GLYCEROL.

Monochlorhydrins, $C_3H_5(OH)_2Cl$. There are two possible isomerides:—

$$\underset{\alpha\text{-Chlorhydrin.}}{CH_2(OH).CH(OH).CH_2Cl} \quad \text{and} \quad \underset{\beta\text{-Chlorhydrin.}}{CH_2(OH).CHCl.CH_2.OH.}$$

α-**Chlorhydrin** is produced, together with a little of the β-variety, on heating glycerol and hydrochloric acid to 100°. It is best prepared by heating epichlorhydrin (p. 456) with water (1 molecule) to 120° (*Berichte*, 13, 457). It is a thick liquid, soluble in water, alcohol and ether; it boils with partial decomposition at 215°. Sodium amalgam converts it into propylene glycol; and when oxidized, it becomes β-chlorlactic acid.

β-Chlorhydrin is obtained from allyl alcohol by the addition of hypochlorous acid. It boils at 230°.

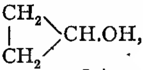
Dichlorhydrins, $C_3H_5(OH)Cl_2$ (*Dichlorpropyl Alcohols*):—

$CH_2Cl.CH(OH).CH_2Cl$ and $CH_2Cl.CHCl.CH_2.OH$.
α-Dichlorhydrin. β-Dichlorhydrin.

α-Dichlorhydrin is produced by the action of hydrochloric acid or chloride of sulphur upon glycerol. It is obtained perfectly pure by shaking epichlorhydrin (p. 456) with concentrated hydrochloric acid.

Preparation.—Saturate a mixture of glycerol (3 parts) and glacial acetic acid (2 parts) with hydrochloric acid gas, accelerating the absorption toward the end by applying heat. The strongly fuming product is washed with a soda solution and the separated oil distilled. The portion going over from 160–200° contains α-dichlorhydrin and acetochlorhydrin. These are difficult to separate (*Annalen*, 208, 361). Therefore, epichlorhydrin is first prepared from the crude dichlorhydrin by adding pulverized caustic soda gradually to the portion which distils at 170–180°, so that the temperature does not exceed 130°. The resulting epichlorhydrin is distilled off (*Berichte*, 10, 557) and changed to α-dichlorhydrin by shaking with concentrated hydrochloric acid.

α-Dichlorhydrin is a liquid, with ethereal odor, of sp. gr. 1.367 at 19°, and boils at 174°. It is not very soluble in water (in 9 parts at 19°), but dissolves readily in alcohol and ether. When heated with hydriodic acid it becomes isopropyl iodide; sodium amalgam produces isopropyl alcohol. Chromic acid oxidizes it to β-dichloracetone (p. 205) and chloracetic acid.

When sodium acts on an ethereal solution of α-dichlorhydrin, we do not get trimethylene alcohol,  but allyl alcohol as a result of molecular transposition (*Berichte*, 21, 1289).

β-Dichlorhydrin, $CH_2Cl.CHCl.CH_2.OH$, obtained by adding chlorine to allyl alcohol, or hypochlorous acid to allyl chloride, boils at 182–183°; its sp. gr. = 1.379 at 0°. Sodium converts it into allyl alcohol. Fuming nitric acid oxidizes it to αβ-dichlorpropionic acid.

Both dichlorhydrins are changed to epichlorhydrin by the alkalies.

Trichlorhydrin, $C_3H_5Cl_3$, is made by the action of PCl_5 upon both dichlorhydrins, and has already been described, p. 104, as glyceryl trichloride.

α-Monobromhydrin, $C_3H_5(OH)_2Br$, is formed when HBr acts on glycerol. It is an oily liquid, which boils at 180° under diminished pressure (*Berichte*, 21, 2890).

α-Dibromhydrin, $CH_2Br.CH(OH).CH_2Br$, is an ethereal-smelling liquid, which boils at 219°; its sp. gr. at 18° is 2.11.

β-Dibromhydrin, $CH_2Br.CHBr.CH_2.OH$, boils at 212–214°.

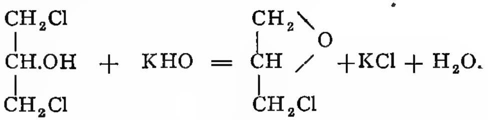
Tribromhydrin, $C_3H_5Br_3$, is described on p. 104. **α-Monoiodhydrin**, $C_3H_5(OH)_2I$, is obtained by heating glycerol and HI to 100°; it is a thick liquid of sp. gr. 1.783.

α-Di-iodhydrin, $CH_2I.CH(OH).CH_2I$, is prepared by heating α-dichlorhydrin with aqueous potassium iodide. A thick oil of specific gravity 2.4 and solidifying at —15°.

GLYCIDE COMPOUNDS.

By this designation we understand certain compounds formed from glycerol derivatives by the exit of H_2O or HCl. These are again readily converted into glycerol derivatives.

Epichlorhydrin, C_3H_5OCl, is isomeric with monochloracetone, and obtained from both dichlorhydrins (p. 455) by the action of caustic potash or soda (analogous to the formation of ethylene oxide from glycolchlorhydrin, (p. 302):—

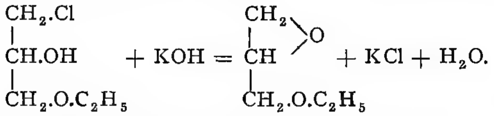


$$\begin{matrix}CH_2Cl\\|\\CH.OH\\|\\CH_2Cl\end{matrix} + KHO = \begin{matrix}CH_2\\|\\CH\\|\\CH_2Cl\end{matrix}\!\!>O + KCl + H_2O.$$

It is a very mobile liquid, insoluble in water and boils at 117°. Its sp. gravity at 0° is 1.203. Its odor resembles that of chloroform, and its taste is sweetish and burning. It forms α-dichlorhydrin with concentrated hydrochloric acid. PCl_5 converts it into trichlorhydrin. Continued heating with water to 180° changes it to α-monochlorhydrin. Concentrated nitric acid oxidizes it to β-chlorlactic acid.

Like ethylene oxide, epichlorhydrin combines with sodium bisulphite, and with CNH to the oxycyanide, $C_3H_5Cl\left\langle\begin{matrix}OH\\CN\end{matrix}\right.$. Hydrochloric acid changes the latter to an acid. **Epicyanhydrin**, $C_3H_5.O.CN$, is formed when CNK acts on epichlorhydrin. Brilliant crystals which fuse at 162.3°, and become **Epihydrin-carboxylic Acid**, $C_3H_5O.CO_2H$, under the influence of HCl (*Berichte*, 15, 2586).

The ethers of chlorhydrin, like $C_3H_5Cl(OH)O.C_2H_5$, are produced on warming epichlorhydrin with alcohols. When they are distilled with caustic potash *glycide ethers* appear:



$$\begin{matrix}CH_2.Cl\\|\\CH.OH\\|\\CH_2.O.C_2H_5\end{matrix} + KOH = \begin{matrix}CH_2\\|\\CH\\|\\CH_2.O.C_2H_5\end{matrix}\!\!>O + KCl + H_2O.$$

Ethyl Glycide Ether, $C_3H_5O.O.C_2H_5$ (Epiethylin), boils at 126-130°; **amyl glycide ether**, $C_3H_5O.O.C_5H_{11}$, at 188°.

Acetic Glycide Ester, $C_3H_5O.O.C_2H_3O$, is produced by heating epichlorhydrin with anhydrous potassium acetate. It boils at 168–169°.

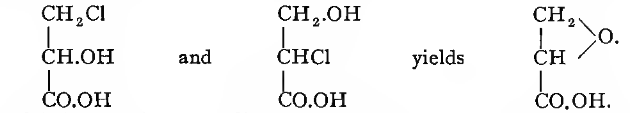
Glycide Alcohol, $C_3H_5O.OH$, is formed by the decomposition of its acetate by caustic soda or baryta. It boils near 162° and is miscible with water, alcohol and ether; its specific gravity is 1.165 at 0°. It reduces ammoniacal silver solutions at ordinary temperatures. This is also true of its acetic ester.

When epichlorhydrin is heated with sodium acetate and absolute alcohol, the reaction proceeds as follows:—

$$C_3H_5OCl + C_2H_3O_2Na + C_2H_5.OH = C_3H_5O.OH + C_2H_3O_2.C_2H_5 + NaCl$$

The glycide formed at first condenses to polyglycides, chiefly diglycide $(C_3H_5O.OH)_2$, which boils at 250° (p. 459).

Glycidic Acid, $C_3H_4O_3$, an oxide or anhydridic acid, is formed (similar to epichlorhydrin) from β-chlorlactic acid and α-chlorhydracrylic acid, when treated with alcoholic potash or soda:—



β-Chlorlactic Acid. α-Chlorhydracrylic Acid. Glycidic Acid.

When separated from its salts by sulphuric acid, it is a mobile liquid, miscible with water, alcohol and ether. It volatilizes when heated and possesses a pungent odor. Its *potassium salt*, $C_3H_3KO_3 + \frac{1}{2}H_2O$, forms warty, crystalline aggregates. Ferrous sulphate does not color the acid or its salts red (distinction from the isomeric pyroracemic acid). It combines with haloid acids to form β-halogen lactic acids, and on warming yields glyceric acid.

Its *ethyl ester*, obtained by the action of ethyl iodide upon its silver salt, is a liquid, with an odor resembling that of malonic ester. It boils at 162°.

See p. 461 for the homologous glycidic acids.

Epibromhydrin, C_3H_5OBr, from the dibromhydrins, is analogous to epichlorhydrin and boils at 130–140°.

Epi-iodhydrin, C_3H_5OI, results from the treatment of epichlorhydrin with a solution of potassium iodide, and boils at 160°.

ALCOHOL ETHERS OF GLYCEROL.

Mixed ethers of glycerol with alcohol radicals (p. 299) are obtained by heating the mono- and dichlorhydrins with sodium alcoholates:—

$$C_3H_5\left\{\begin{matrix}OH\\Cl_2\end{matrix}\right. + 2C_2H_5.ONa = C_3H_5\left\{\begin{matrix}OH\\(O\,C_2H_5)_2\end{matrix}\right. + 2NaCl.$$

Monoethylin, $C_3H_5\left\{\begin{matrix}(OH)_2\\O.C_2H_5\end{matrix}\right.$, is soluble in water, and boils at 230°. **Diethylin,** $C_3H_5\left\{\begin{matrix}OH\\(O.C_2H_5)_2\end{matrix}\right.$, dissolves with difficulty in water, has an odor resembling that of peppermint, and boils at 191°; its specific gravity is 0.92. When its sodium compound is treated with ethyl iodide we obtain *Triethylin*, $C_3H_5(O.C_2H_5)_3$, insoluble in water and boiling at 185°.

Allylin, $C_3H_5\left\{\begin{matrix}(OH)_2\\O.C_3H_5\end{matrix}\right.$, monoallyl ether, is produced by heating glycerol with oxalic acid, and is present in the residue from the preparation of allyl alcohol (p. 134). It is a thick liquid, boiling at 225–240°.

A compound of the formula, $C_6H_{10}O_3$, and designated *glycerin ether*, $(C_3H_6)_2O_3$, occurs with allylin, and boils at 169–172° (see *Berichte*, 14, 1496 and 2270).

ACID ESTERS OF GLYCEROL.

By replacing 1, 2 and 3 hydrogen atoms in glycerol with acid radicals we obtain the so-called *mono-*, *di-*, and *triglycerides.* They are formed when glycerol and fatty acids are heated to 100–300°; whereas in the action of acid chlorides upon glycerol, esters of the chlorhydrins (p. 455) are produced :—

$$C_3H_5(OH)_3 + C_2H_3O.Cl = C_3H_5Cl(OH)(O.C_2H_3O) + H_2O.$$

When the acid glycerides are acted upon with alkalies, lime water, or lead oxide, they all revert to glycerol and salts of the fatty acids (soap) (p. 216). Concentrated sulphuric acid decomposes them into free acids and glycerol sulphuric acid (p. 454).

Monoformic Ester, $C_3H_5\left\{\begin{matrix}(OH)_2\\O.CHO\end{matrix}\right.$, Monoformin, is produced by heating glycerol with oxalic acid (p. 217). It distils near 200°, and decomposes partly into allyl alcohol, carbon dioxide and water; it distils without decomposition in a vacuum.

Monacetin, $C_3H_6\left\{\begin{matrix}(OH)_2\\O.C_2H_3O\end{matrix}\right.$, is formed on heating glycerol with glacial acetic acid to 100°. It is a liquid which dissolves readily in water and ether. *Diacetin,* $C_3H_5\left\{\begin{matrix}OH\\(O.C_2H_3O)_2\end{matrix}\right.$, is obtained from glycerol and glacial acetic acid when they are heated to 200°. It boils at 280°.

Triacetin, $C_3H_5(O.C_2H_3O)_3$, is prepared by prolonged heating of diacetin with an excess of glacial acetic acid to 250°; it boils at 268°. It is found in slight quantities in the oil of *Euonymus europæus.*

Tributyrin, $C_3H_5(O.C_4H_7O)_3$, occurs along with other higher triglycerides in cow's butter.

The glycerides of the higher fatty acids, $C_nH_{2n}O_2$, and those of the oleïc acid series, $C_nH_{2n-2}O_2$, occur in the natural fatty oils, fats, and tallows; they can be obtained artificially by heating glycerol with the acids.

Monopalmitin, $C_3H_5\left\{\begin{matrix}(OH)_2\\O.C_{16}H_{31}O\end{matrix}\right.$, melts at 58°. **Dipalmitin,** $C_3H_5\left\{\begin{matrix}OH\\(O.C_{16}H_{31}O)_2\end{matrix}\right.$, at 59°. **Tripalmitin,** $C_3H_5(O.C_{16}H_{31}O)_3$, is found in most fats, especially in palm oil, from which it can be obtained by strong pressing and recrystallization from ether. It separates from olive oil when the latter is strongly cooled. It crystallizes from ether in pearly, glistening laminæ, which melt at 63°. By repeated fusion and solidification the melting point falls quite considerably. Like all higher triglycerides, it is not very soluble in alcohol.

Trimyristin, or **Myristin,** $C_3H_5(O.C_{14}H_{27}O)_3$, glycerol myristic ester, occurs in spermaceti, in muscat butter, and chiefly in oil nuts (from Myristica surinamensis), from which it is most readily obtained (*Berichte*, 18, 2011). It crystallizes from ether in glistening needles, melting at 55°. It yields myristic acid (p. 215) when saponified.

Tristearin, $C_3H_5(O.C_{18}H_{35}O)_3$, occurs mainly in solid fats (tallows). It can be obtained by heating glycerol and stearic acid to 280–300°. It crystallizes from ether in shining leaflets, and melts at 66.5°. Its melting point is also lowered by repeated fusion.

Trioleïn, $C_3H_5(O.C_{18}H_{33}O)_3$, is found in oils, like olive oil. It solidifies at —6°. It is oxidized on exposure to the air. Nitrous acid converts it into the isomeric elaïdin, which melts at 36° (p. 243).

Nearly all the natural fatty oils and fats (tallows) of animal and vegetable origin are mixtures of the triglycerides of the fatty acids. The former are chiefly trioleïn, the latter (beef tallow, sheep tallow, cocoa butter, etc.), tristearin and tripalmitin. They are insoluble in water, dissolve with difficulty in alcohol, readily in ether, carbon disulphide, benzene ether, etc. They are lighter than water and swim upon it. They form spots on paper which do not disappear when heated—distinction from the *volatile oils*. They are not volatile, and decompose when strongly heated.

The fatty oils are distinguished as *drying* and *non-drying oils*. The former oxidize readily in the air, are coated with a film and become solid; they comprise the glycerides of the unsaturated acids—linoleic and ricinoleic acids (p. 243). The non-drying oils are glycerides of oleic acid; the production of free acid in them is the cause of their becoming rancid. Among the drying oils are *linseed oil, hemp oil, walnut oil, castor oil*, etc. Non-drying oils are olive oil, rape-seed oil (from *Brassica campestris*), also from the oil of *Brassica rapa*, almond oil, train oil and cod oil.

Boiling alkalies saponify all the fats.

SULPHUR DERIVATIVES OF GLYCEROL.

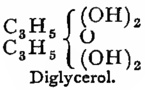
Glycerol mercaptans are formed on heating the chlorhydrins with an alcoholic solution of potassium sulphydrate;—

$$C_3H_5Cl_3 + 3KSH = C_3H_5(SH)_3 + 3KCl.$$

The hydrogen atoms in the SH groups can be replaced by heavy metals. Hydrochloric acid precipitates them in the form of thick oils. When oxidized they yield sulpho-acids, which may be prepared from the chlorhydrins by means of alkaline sulphites.

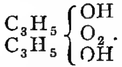
POLYGLYCEROLS.

They are obtained like the polyglycols (p. 304), viz., by the union of several molecules of glycerol and withdrawal of water. To obtain them, glycerol (diluted ⅓ with water), is saturated with HCl and heated to 130° for some hours; or glycerol and monochlorhydrin are heated together. They are thick liquids, which can be separated from each other by distillation under diminished pressure. When heated with solid caustic potash they sustain further loss of water and become polyglycides (p. 457):—



$$\begin{matrix}C_3H_5\\C_3H_5\end{matrix}\left\{\begin{matrix}(OH)_2\\O\\(OH)_2\end{matrix}\right.$$

Diglycerol.



$$\begin{matrix}C_3H_5\\C_3H_5\end{matrix}\left\{\begin{matrix}OH\\O_2\\OH\end{matrix}\right. .$$

Diglycide.

Of the higher trihydric alcohols which have been prepared, we have: **Butyl glycerol**, $C_4H_{10}O_3 = CH_3.CH(OH).CH(OH).CH_2.OH$, from the bromide of crotyl alcohol, by boiling it with water. It is a thick, sweet liquid, boiling at 172–175° under 27 mm. pressure.

Hexyl Glycerol, $C_6H_{14}O_3$. There are three isomeric derivatives of this class, obtained from the corresponding unsaturated, monohydric alcohols, $C_6H_{12}O$, by the addition of bromine, and then boiling with water. They are thick liquids, readily soluble in water (*Berichte*, 22, Ref. 788).

Other glycerols have been obtained by oxidizing unsaturated monohydric alcohols with potassium permanganate (p. 451).

MONOBASIC ACIDS, $C_nH_{2n}O_4$.

The acids of this series bear the same relation to the glycerols, that the lactic acids bear to the glycols. They, too, can be regarded as dioxy-fatty acids (p. 345).

They may be synthetically prepared by the common methods used in the production of oxyacids (p. 346), also by oxidizing unsaturated acids with potassium permanganate (p. 236) (*Berichte*, 31, Ref. 660).

The first and lowest dioxyacid (p. 330) has been described as *glyoxylic acid*, (dioxyacetic acid). Both free and in its salts it has one molecule of water firmly combined: $CHO.COOH + H_2O = CH(OH)_2.CO_2H$. However, the two hydroxyl groups do not manifest the usual reactions, but split off water with formation of the aldehyde group.

Glyceric Acid, $C_3H_6O_4$ (dioxypropionic acid), s formed: (1) by the careful oxidation of glycerol with nitric acid:—

$$CH_2(OH).CH(OH).CH_2(OH) + O_2 = CH_2(OH).CH(OH).CO.OH + H_2O;$$

(2) by the action of silver oxide upon β-chlorlactic acid, $CH_2Cl.CH(OH).CO_2H$, and α-chlorhydracrylic acid, $CH_2(OH).CHCl.CO_2H$ (p. 457); (3) by heating glycidic acid with water (p. 457).

Preparation.—A mixture of 1 volume of glycerol and 1 volume of water is placed in a tall glass cylinder and then 1 part HNO_3 (sp. gr. 1.5) is introduced by means of a funnel whose end reaches to the bottom of the vessel. Two layers of liquid form and the mixture is permitted to stand for several days at 20°, until the layers have completely united. The liquid is then evaporated to syrup consistence, diluted with water, saturated while boiling with calcium carbonate and some lime water added, to precipitate any impurities. When the filtrate is concentrated calcium glycerate separates in warty crusts. It is decomposed with oxalic acid, filtered from the separated oxalate and the filtrate boiled with lead oxide to remove all excess of oxalic acid. Hydrogen sulphide precipitates the lead in this filtrate and the liquid is then concentrated upon a water bath (*Berichte*, 9, 1902, 10, 267, 14, 2071).

The acid may be obtained in small quantities by oxidizing glycerol with mercuric oxide and baryta water (*Berichte*, 18, 3357).

Glyceric acid forms a syrup which cannot be crystallized. It is easily soluble in water and alcohol. It is optically inactive, but as it contains an asymmetrical carbon atom (p. 63), it may be changed to active lævo-rotatory glyceric acid by the fermentation of its ammonium salt, through the agency of Penicillium glaucum (p. 357).

Its *calcium salt* $(C_3H_5O_4)_2Ca + 2H_2O$, crystallizes in warty masses, consisting of concentrically grouped needles. It dissolves readily in water but not in alcohol. The *lead salt*, $(C_3H_5O_4)_2Pb$, is not very soluble in water. The *ethyl ester*, $C_3H_5O_4.C_2H_5$, is formed on heating glyceric acid with absolute alcohol. It is a thick liquid of sp. gr. 1.193 at 0°, and boils at 230–240°.

When the acid is heated to 140° it decomposes into water, pyroracemic and pyrotartaric acids. When fused with potash it forms acetic and formic acids, and when boiled with it yields oxalic and lactic acids. Phosphorus iodide converts it into β-iodpropionic acid. Heated with hydrochloric acid it yields α-chlorhydracrylic acid and αβ-dichlorpropionic acid.

When glyceric acid is preserved awhile it forms an ester-like modification or anhydride, $(C_3H_4O_3)_2$ (?). This is sparingly soluble and crystallizes in fine needles. When boiled with water it again reverts to the original acid.

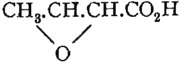
Amido-glycerol, or Serin, $CH_2(OH).CH(NH_2).CO_2H$, α-amidohydracrylic acid, is obtained by boiling serecin with dilute sulphuric acid. It forms hard crystals, soluble in 24 parts of water at 20°, but insoluble in alcohol and ether. Being an amido-acid it has a neutral reaction, but combines with both acids and bases. Nitrous acid converts it into glyceric acid.

Isomeric *β-amido-lactic acid*, $CH_2(NH_2).CH(OH).CO_2H$, is obtained from β-chlorlactic acid and glycidic acid by the action of ammonia (*Berichte*, 13, 1077). It dissolves with more difficulty in water than serin.

The **Hydrate** of trichlorpyroracemic acid, $CCl_3.CO.CO_2H + H_2O$, may be considered as **isotrichlorglyceric acid,** $CCl_3.C(OH)_2.CO_2H$. It is formed from trichloracetyl cyanide, $CCl_3.CO.CN$, by the action of hydrochloric acid (p. 332). It crystallizes in long needles, melts at 102° and distils undecomposed. It reduces ammoniacal silver solutions and alkaline copper solutions. An interesting method of forming it (along with tricarballylic acid) consists in the action of $KClO_3$ and hydrochloric acid upon gallic acid, salicylic acid and phenol (*Berichte*, 13, 1938).

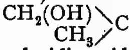
Mention may be made of the following higher dioxyacids:—

The dioxybutyric acids, $C_4H_8O_4$, are known in three isomeric forms:

(1) **αβ-Dioxybutyric Acid,** $CH_3.CH(OH).CH(OH).CO_2H$, **β-Methylglyceric Acid,** is prepared from αβ-dibrombutyric acid on boiling it with water, or upon digesting β-methyl glycidic acid (see below) with water. A thick liquid, gradually becoming solid and crystalline. It melts at 80° C. Its corresponding *β-Methyl glycidic acid*,  $CH_3.\underset{\diagdown\, O\, \diagup}{CH.CH}.CO_2H$ (p. 457), has been obtained from chloroxybutyric acid (m. p. 62–63°, from normal crotonic acid and ClOH) by the action of alcoholic potash. It crystallizes in rhombic prisms, melting at 84°

(*Annalen*, 234, 204). The same acid is also formed from the chloroxybutyric acid melting at 82–85° (from isocrotonic acid by addition of ClOH and from β-methyl glycidic acid with HCl) (*Annalen*, 234, 221). It yields αβ-dioxybutyric acid when heated with water.

(2) **βγ-Dioxybutyric Acid**, $CH_2(OH).CH(OH).CH_2.CO_2H$, butyl glyceric acid, from α-chlorhydrin (p. 454), HCN and HCl, is a thick liquid, which passes into an anhydride (oxybutyrolactone) at 100° C.

(3) **Dioxyisobutyric Acid**,  $\begin{matrix} CH_2(OH) \\ CH_3 \end{matrix}\!\!>C(OH).CO_2H$, α-methyl glyceric acid, results upon warming α-methyl glycidic acid with water to 100°. It crystallizes after long standing and melts at 100°. The α-methyl glycidic acid corresponding to it, has been obtained from chloroxyisobutyric acid (melting at 106–107°, from methacrylic acid p. 457, by addition of ClOH) when acted upon by alcoholic potash. It is a thick liquid. It combines with HCl to form chloroxyisobutyric acid.

The following acids have been obtained by oxidizing unsaturated fatty acids with potassium permanganate:—

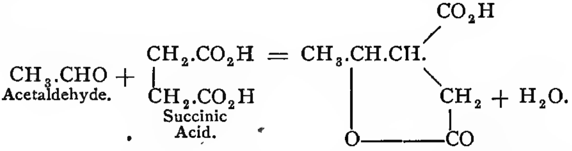
Dioxyundecylic Acid, $C_{11}H_{20}(OH)_2O_2$, from undecylenic acid, $C_{11}H_{20}O_2$, melts at 84–86°.

Dioxybehenic Acid, $C_{22}H_{42}(OH)_2O_2$, from erucic acid, $C_{22}H_{42}O_2$, melts at 133°.

Dioxystearic Acid, $C_{18}H_{34}(OH)_2O_2$, from oleic acid, $C_{18}H_{34}O_2$, melts at 136° (*Berichte*, 22, 743).

DIBASIC OXY-ACIDS, $C_nH_{2n-2}O_5$.

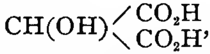
We can regard these as derivatives of the dibasic acids, $C_nH_{2n}(CO_2H)_2$, from which they are obtained by the introduction of one OH-group for one atom of hydrogen (p. 345). Those oxydicarboxylic acids, in which the hydroxyl group occupies the γ-position with reference to one of the two carboxyls, α-oxyglutaric acid (p. 467) excepted, immediately decompose when set free into water,—and lactonic acids or lactone carboxylic acids (see itamalic acid, p. 468). Such lactonic acids can be directly prepared synthetically by digesting the aldehydes with sodium succinate in the presence of acetic anhydride (*Berichte*, 18, 2523; 23, Ref. 85):—



Methyl Paraconic Acid.

Ethyl paraconic acid is formed, in a similar manner, from succinic acid and propionic aldehyde, and propionparaconic acid from succinic acid and butyraldehyde.

The reaction probably proceeds in a manner analogous to that of aldehyde upon aceto-acetic ester and malonic ester. First, unsaturated acids are produced. These undergo a rearrangement of atoms and become lactonic acids. This is analogous to the conversion of allylacetic acid into valerolactone. Or, they can also be obtained from the corresponding unsaturated dicarboxylic acids by molecular transposition (when acted upon by hydrobromic acid) (see allyl malonic acid, p. 430, and allyl succinic acid, p. 430). The aldehydes also react with pyroracemic acid. Two isomeric lactonic acids result (*Berichte*, 23, Ref. 90). When neutralized in the cold with caustic alkali, or with alkaline carbonates, the lactonic acids from the oxydicarbonic acids usually form monobasic salts with the free carboxyl group, whereas when boiled with alkalies dibasic salts of the oxydicarboxylic acids result. Heated alone, or when boiled with dilute sulphuric acid, the lactonic acids split up into CO_2 and lactones, which are in part converted into the isomeric $\beta\gamma$-unsaturated acids (p. 352); unsaturated dibasic acids are formed at the same time. The lactonic acids derived from pyroracemic acid yield carbon dioxide and unsaturated hydrocarbons when they are distilled. Lactones and unsaturated acids are also formed (*Berichte*, 23, Ref. 91).



1. **Tartronic Acid**, $C_3H_4O_5 = CH(OH)\left\langle\begin{matrix}CO_2H\\CO_2H\end{matrix}\right.$, oxymalonic acid, is produced from chlor- and brom-malonic acid, $CHCl(CO_2H)_2$, by the action of silver oxide or by saponifying their esters with alkalies; from mesoxalic acid, $CO(CO_2H)_2$, by the action of sodium amalgam; from dibrompyroracemic acid, $CHBr_2.CO.CO_2H$, when digested with baryta water; from glycerol by oxidation with potassium permanganate. Also from glyoxylic acid, $CHO.CO_2H$, by the action of CNH and hydrochloric acid, and from nitro-tartaric acid, and dioxytartaric acid, as well as from trichlorlactic acid when the latter is digested with alkalies.

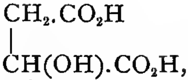
Preparation.—Nitrotartaric acid is gradually introduced into warm aqueous alcohol (*Berichte*, 10, 1789). A better method consists in adding trichlorlactic ester (p. 360) to a warm sodium hydroxide (4 molecules) solution. After acidulation with acetic acid barium chloride is added to precipitate barium tartronate, and this is then decomposed with sulphuric acid. To obtain the ethyl ester mix the barium tartronate with alcohol and saturate with hydrochloric acid gas (*Berichte*, 18, 754, 2852).

Tartronic acid is easily soluble in water, alcohol and ether, and crystallizes in large prisms. When pure it melts at 184°, decomposing into carbon dioxide and glycolide, $(C_2H_2O_2)_2$ (*Berichte*, 18, 756).

The *calcium salt*, $C_3H_2O_5Ca$, and *barium salt*, $C_3H_2O_5Ba + 2H_2O$, dissolve with difficulty in water and are obtained as crystalline precipitates. The *ethyl ester*, $C_3H_2O_5(C_2H_5)_2$ (see above) is a liquid boiling at 219°.

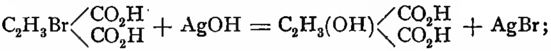
Tartramic Acid, $CH(NH_2).(CO_2H)_2$, was described on p. 409 as amidomalonic acid.

2. **Malic Acid**, $C_4H_6O_5 =$



$$\begin{array}{l} CH_2.CO_2H \\ | \\ CH(OH).CO_2H, \end{array}$$

Oxysuccinic Acid, (*Acidum malicum*), occurs free or in the form of salts in many plant juices, in unripe apples, in grapes and in mountain-ash berries (from *Sorbus aucuparia*). It is artificially prepared by the action of nitrous acid upon asparagine or aspartic acid (p. 466); by boiling bromsuccinic acid with silver oxide:—



$$C_2H_3Br\left\langle\begin{array}{l} CO_2H \\ CO_2H \end{array}\right. + AgOH = C_2H_3(OH)\left\langle\begin{array}{l} CO_2H \\ CO_2H \end{array}\right. + AgBr;$$

by the reduction of tartaric and racemic acids with hydriodic acid (p. 411); by heating fumaric acid with caustic soda to 100° or with water to 200°; and by saponifying the esters of chlorethenyltricarboxylic acid (p. 471).

The best source of malic acid is the juice of unripe mountain-ash berries. This is concentrated, filtered, and while boiling saturated with milk of lime. The pulverulent lime salt which separates is dissolved in hot dilute nitric acid (1 part HNO_3 in 10 parts water); on cooling acid calcium malate crystallizes from the liquid. To obtain the pure acid, the lead salt is prepared and decomposed with hydrogen sulphide (*Annalen*, 38, 259).

Malic acid forms deliquescent crystals, which dissolve readily in alcohol, slightly in ether, melt at 100°, and at 140° lose water and pass into fumaric and maleïc acids (p. 425).

It exists in three different modifications; these are identical in structure (*Berichte*, **18**, 2170, 2713). They are chiefly distinguished by their optical deportment. As malic acid contains an asymmetric carbon atom, it is possible for it, according to van't Hoff's theory, to appear in three forms—a lævo-rotatory, a dextro-rotatory, and an inactive (para) form. The latter can be resolved into the active varieties.

The natural malic acid (from mountain-ash berries) rotates the plane of polarization to the left, that obtained from dextrotartaric acid and aspartic acid turns it to the right ($[\alpha]_D = 3.3°$). The variety obtained from fumaric and chlorethenyltricarboxylic acids is inactive and melts at 130–135° (*Annalen*, **214**, 50). The inactive acid, formed in the reduction of racemic acid, fumaric acid and maleïc acid, can be resolved, by means of the cinchonine salt, into a dextro- and lævo-rotatory malic acid (*Berichte*, **18**, Ref. 537).

Succinic acid is formed by the reduction of malic acid. This is accomplished by the fermentation of the lime salt with yeast, or by heating the acid with hydriodic acid to 130° (p. 411). When it is warmed with hydrobromic acid, it forms monobrom-succinic acid. Bromine converts malic acid into bromoform and carbon dioxide.

When the acid is heated to 180° it decomposes into water, fumaric acid, maleïc acid and maleïc anhydride (p. 427). The coumarines are produced when the acid is heated with phenols and sulphuric acid. This result is probably to be explained by assuming that the malic acid first changes to the first aldehyde of malonic acid, $CHO.CH_2.CO_2H$, and this then condenses with the phenols (*Berichte*, 17, 1647). When malic acid is heated alone, or with sulphuric acid or zinc chloride, the product is cumalic acid (see this).

The neutral *alkali malates* do not crystallize well and soon deliquesce; the primary salts, however, do crystallize. The *primary ammonium salt*, $C_4H_5(NH_4)O_5$, forms large crystals, and when exposed to a temperature of 160–200°, becomes *fumarimide*, $C_4H_2O_2.NH$.

Neutral Calcium Malate, $C_4H_4O_5Ca + H_2O$, separates as a crystalline powder on boiling. The acid salt, $(C_4H_5O_5)_2Ca + 6H_2O$, forms large crystals which are not very soluble (*Berichte*, 19, Ref. 679). Sugar of lead precipitates an amorphous *lead salt* from the aqueous solution. This melts in boiling water.

Sodium Brommalate (from the acid, $C_4H_5BrO_5$), is formed when the aqueous solution of sodium dibromsuccinate is boiled; milk of lime transforms it into tartaric acid.

The *diethyl ester*, $C_4H_4(C_2H_5)_2O_5$, suffers partial decomposition when boiled. Acetyl chloride converts it into ethyl aceto-malate, $C_2H_3\left\{\begin{array}{l}O.C_2H_3O\\(CO_2.C_2H_5)_2\end{array}\right.$, which boils at 258°.

Consult *Berichte*, 18, 1952, for the boiling temperatures of the malic acid esters.

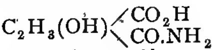
As an isomeride of malic acid, may be mentioned:—

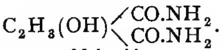
α-**Oxyisosuccinic Acid**, $CH_3.C(OH).(CO_2H)_2$, Methyl Tartronic Acid, which is formed from pyroracemic acid, $CH_3.CO.CO_2H$, by means of CNH, etc. Isomalic acid, obtained from bromisosuccinic acid by the action of silver oxide, is probably identical with the preceding. Both decompose at 178° into carbon dioxide and α-lactic acid.

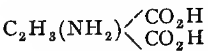
Its *ethyl ester*, $CH_3.C(O.C_2H_5)(CO_2H)_2$, and not methylene-malonic acid (p. 428), is formed when bromisosuccinic acid is acted upon with alcoholic potash.

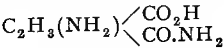
β-Oxyisosuccinic Acid, $CH_2.OH.CH.(CO_2H)_2$. Its ethyl ester is produced when methylene-malonic ester (p. 428) is saponified with alcoholic potash (*Berichte*, 23, Ref. 194).

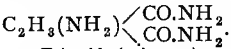
Amides of Malic Acid:—


Malamic Acid.


Malamide.

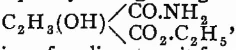

Aspartic Acid.

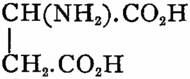

Asparagine.


Triamide (unknown).

Aspartic acid bears the same relation to malic and succinic acids, as glycocoll bears to glycollic acid and acetic acid (p. 366); hence, it may be called amidosuccinic acid.

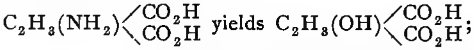
Malamide, $C_4H_8O_3N_2$, is formed by the action of ammonia upon dry ethyl malate. It forms large crystals. When heated with water, it breaks up into malic acid and ammonia, thus plainly distinguishing itself from isomeric asparagine.

Ethyl Malamate, 
$C_2H_3(OH)\begin{cases} CO.NH_2 \\ CO_2.C_2H_5 \end{cases}$, is obtained by leading ammonia into the alcoholic solution of malic ester; it forms a crystalline mass.

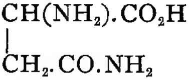
Aspartic Acid, $C_4H_7NO_4 =$ 
$$\begin{array}{l} CH(NH_2).CO_2H \\ | \\ CH_2.CO_2H \end{array}$$
, **amidosuccinic acid,** occurs in the vinasse obtained from the beet root, and is procured from albuminous bodies in various reactions. It is prepared by boiling asparagine with alkalies and acids (*Berichte*, 17, 2924).

It may be synthetically formed as follows: By the reduction of isonitrososuccinic acid (the oxime of oxalacetic acid, p. 435) with sodium amalgam; by heating fumaric and maleïc esters to 110° with alcoholic ammonia (*Berichte*, 21, 86, 644); and by heating fumarimide and maleïmide with water: $C_4H_2O_2{:}NH + 2H_2O = C_4H_7NO_4$. As it contains an asymmetric carbon atom, it can (like malic acid) exist in a lævo-rotatory, dextro-rotatory and inactive variety. Naturally occurring aspartic acid is lævo-rotatory; it crystallizes in rhombic prisms, or leaflets, and dissolves with difficulty in water (in 256 parts at 10° and in 18 parts at 100°). The synthetic acid is *inactive*. It is more soluble in water, and consists of monoclinic crystals. Active aspartic acid is changed to the inactive form by heating it with hydrochloric acid to 180°. Like glycocoll it combines with alkalies and acids yielding salts; with the former it yields acid and neutral salts, *e. g.*, $C_4H_6NO_4Na + H_2O$ and $(C_4H_6NO_4)_2Ba + 3H_2O$.

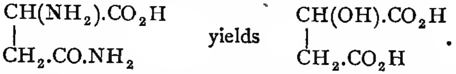
Nitrous acid changes it to malic acid:—


$$C_2H_3(NH_2)\begin{cases} CO_2H \\ CO_2H \end{cases} \text{ yields } C_2H_3(OH)\begin{cases} CO_2H \\ CO_2H \end{cases};$$

from the active variety there results the active malic acid, and from the inactive, the inactive malic modification.

Asparagine, $C_4H_8N_2O_3 =$ 
$$\begin{array}{l} CH(NH_2).CO_2H \\ | \\ CH_2.CO.NH_2 \end{array}$$
, the monamide of aspartic acid, is found in many plants, chiefly in their seeds; in asparagus, in beet-root, in peas and beans, etc. It often crystallizes from the pressed juices of these plants after evaporation. It is artificially produced when bromsuccinic ester is heated to 100° with ammonia (*Berichte*, 20, Ref. 152), or by the action of alcoholic ammonia upon aspartic ester (*Berichte*, 20, Ref. 510; *Berichte*, 22, Ref. 243). Natural asparagine forms shining, four-sided, rhombic prisms, containing one molecule of water, and is readily soluble in hot water, but not in alcohol or ether. Its aqueous solution is lævo-rotatory. *Dextro*-asparagine, from the sprouts of vetches, has been produced on heating inactive aspartic ester with alcoholic ammonia. It differs from ordinary asparagine in having a sweet

taste, and in forming right-hemihedral crystals (*Berichte*, 19, 1691). It forms salts with bases and acids (1 equivalent). It changes to aspartic acid, giving off ammonia, when it is boiled with water; the conversion is more speedy when alkalies or acids are employed. Nitrous acid converts it into malic acid:—



$$\begin{array}{l}\mathrm{CH(NH_2).CO_2H}\\ |\\ \mathrm{CH_2.CO.NH_2}\end{array} \quad \text{yields} \quad \begin{array}{l}\mathrm{CH(OH).CO_2H}\\ |\\ \mathrm{CH_2.CO_2H}\end{array}.$$

It forms ammonium succinate when it ferments in the presence of albuminoids.

α-Amido-isosuccinic Acid, $\mathrm{CH_3.C(NH)_2}\Big\langle\begin{array}{l}\mathrm{CO_2H}\\ \mathrm{CO_2H}\end{array}$, is the only amid-derivative prepared from oxysuccinic or isomalic acid. It has been obtained by the action of hydrocyanic acid and alcoholic ammonia upon pyroracemic acid, $\mathrm{CH_3.CO.CO_2H}$ (*Berichte*, 20, Ref. 507).

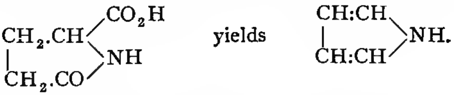
3. OXY-PYROTARTARIC ACIDS, $C_5H_8O_5 = C_3H_5(OH)\Big\langle\begin{array}{l}\mathrm{CO_2H}\\ \mathrm{CO_2H}\end{array}$.

(1) **α-Oxyglutaric Acid**, $\mathrm{CH_2}\Big\langle\begin{array}{l}\mathrm{CH(OH).CO_2H}\\ \mathrm{CH_2.CO_2H}\end{array}$ (*Annalen*, 208, 66, and *Berichte*, 15, 1157), is obtained by the action of nitrous acid upon glutaminic acid; it occurs in molasses. It crystallizes with difficulty, and melts at 72°. Heated with hydriodic acid it yields glutaric acid (p. 417).

Glutaminic Acid, $\mathrm{CH_2}\Big\langle\begin{array}{l}\mathrm{CH(NH_2).CO_2H}\\ \mathrm{CH_2.CO_2H}\end{array} = C_5H_7(NH_2)O_4$, occurs with aspartic acid in the molasses from beet root, and is formed along with other compounds (p. 366) when albuminoid substances are boiled with dilute sulphuric acid. It consists of brilliant rhombohedra, soluble in hot water but insoluble in alcohol and ether. It melts at 140° and suffers partial decomposition. Like all other amido-acids, it forms salts with acids and bases. Mercuric nitrate throws it out of aqueous solution as a white precipitate.

Ordinary glutaminic acid is dextro-rotatory. Upon decomposing the albuminoid conglutin with hydrochloric acid, the ordinary active variety of glutaminic acid is produced, but if the rupture be brought about by baryta water, an *inactive* glutaminic acid is obtained. The latter is converted into lævorotatory glutaminic acid by *Penicillium glaucum* (p. 65) (*Berichte*, 17, 388).

As glutaminic acid is a γ-amido-acid it has power to form an amido-anhydride (a lactam); the resulting (by heating to 190°) **Pyroglutaminic Acid**, $C_5H_7NO_3$, yields pyrrol, C_4H_5N (*Berichte*, 15, 1222), when heated further:—

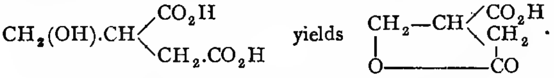


Glutamin, $C_3H_5(NH_2)\Big\langle\begin{array}{l}\mathrm{CO.NH_2}\\ \mathrm{CO_2H}\end{array}$, the amide of amido-glutaric acid, corresponding to asparagine, occurs together with this in beet sprouts. It crystallizes in needles. When digested with baryta water, glutamin changes to amido-glutaric acid.

(2) **β-Oxyglutaric Acid,** $CH(OH)\left\langle\begin{matrix}CH_2.CO_2H\\CH_2.CO_2H\end{matrix}\right.$, is obtained from α-dichlorhydrin (p. 455) by means of potassium cyanide. It forms crystals which dissolve easily in water, alcohol and ether, and melt at 135°.

(3) **α-Oxypyrotartaric Acid,** $CH_3.C(OH)\left\langle\begin{matrix}CH_2.CO_2H\\CO_2H\end{matrix}\right.$, is produced by the action of hydrocyanic and hydrochloric acids upon ethyl aceto-acetate, or by oxidizing isovaleric acid with nitric acid (p. 347). It forms a thick syrup, which solidifies in a vacuum and then melts at 108°. Near 200° it decomposes into water and citraconic anhydride.

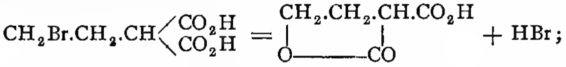
(4) **Itamalic Acid** is only stable in its salts. When free, it decomposes into water and **Paraconic Acid,** $C_5H_6O_4$ (*Annalen*, 218, 77):—



Itamalic Acid. Paraconic Acid.

Calcium itamalate is obtained by boiling itachlorpyrotartaric acid (p. 418) with calcium carbonate. Paraconic acid is best prepared by boiling itabrom-pyrotartaric acid with water. It is very deliquescent and melts at 57-58°. When boiled with bases, it forms salts of itamalic acid; it yields citraconic anhydride when it is distilled.

(5) **γ-Oxy-ethyl Malonic Acid,** $CH_2(OH).CH_2.CH(CO_2H)_2$. Butyrolactone carboxylic acid is its lactone acid. This is obtained from brom-ethylmalonic acid (melting at 117°—from vinyl malonic acid = trimethylene dicarboxylic acid) when heated with water:—



and when isomeric vinaconic acid (α-trimethylene dicarboxylic acid) is digested with dilute sulphuric acid (p. 352) (*Annalen*, 227, 13).

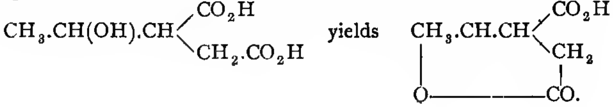
Heated to 120° it breaks up into carbon dioxide and butyrolactone (p. 362).

(6) **Citramalic Acid,** $C_3H_5(OH)\left\langle\begin{matrix}CO_2H\\CO_2H\end{matrix}\right.$, is obtained by the action of zinc and hydrochloric acid upon chlorcitramalic acid, $C_5H_7ClO_5$ (by addition of ClOH to citraconic acid). Large crystals, melting at 119° and decomposing at 130° into water and citraconic acid.

(7) **Ethyl Tartronic Acid,** $C_2H_5.C(OH)\left\langle\begin{matrix}CO_2H\\CO_2H\end{matrix}\right.$, is obtained by chlorinating ethyl malonate, $C_2H_5.CH(CO_2H)_2$, and subsequently saponifying it with baryta water (p. 409). It melts at 98° and at 180° decomposes into carbon dioxide and α-oxybutyric acid.

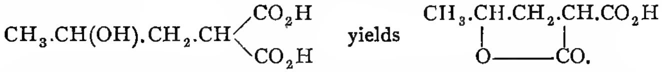
4. Acids, $C_6H_{10}O_5$.

(1) **Methyl Itamalic Acid,** $C_6H_{10}O_5$, and **Methyl Paraconic Acid,** $C_6H_8O_4$,



Methyl paraconic acid is produced when acetaldehyde and sodium succinate are heated with acetic anhydride (p. 463). It crystallizes from benzene in needles or leaflets. It melts at 79°, and resolidifies at 84°. It unites with bases, in the cold, to form salts of the formula, $\mathrm{C_6H_7O_4M\acute{e}}$. When it is boiled with bases salts of methyl itamalic acid are produced : $\mathrm{C_6H_8O_5M\acute{e}_2}$. When distilled methyl paraconic acid yields valerolactone, ethylidene propionic acid (p. 241), methylitaconic acid and methyl citraconic acid (p. 463 and *Berichte*, 24, Ref. 91).

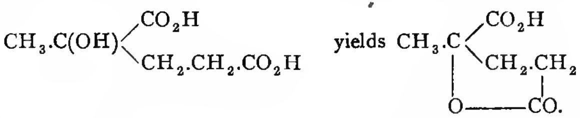
(2) **Oxypropyl Malonic Acid,** $\mathrm{C_6H_{10}O_5}$, and **α-Carbovalerolactonic Acid,** $\mathrm{C_6H_8O_4}$:—



$$\mathrm{CH_3.CH(OH).CH_2.CH}\begin{cases}\mathrm{CO_2H}\\ \mathrm{CO_2H}\end{cases}\quad\text{yields}\quad\begin{array}{l}\mathrm{CH_3.CH.CH_2.CH.CO_2H}\\ \qquad\quad |\qquad\qquad\ |\\ \qquad\ \mathrm{O}\text{———}\mathrm{CO.}\end{array}$$

The second acid has been prepared from allyl malonic acid (p. 430). At 200° it decomposes into valerolactone and carbon dioxide (p. 363).

(3) **Methyl Oxyglutaric Acid,** $\mathrm{C_6H_{10}O_5}$, and **γ-Carbovalerolactonic Acid,** $\mathrm{C_6H_8O_4}$:—

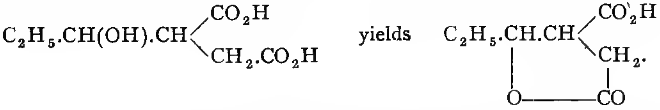


$$\mathrm{CH_3.C(OH)}\begin{cases}\mathrm{CO_2H}\\ \mathrm{CH_2.CH_2.CO_2H}\end{cases}\quad\text{yields}\quad\begin{array}{l}\mathrm{CH_3.C}\begin{cases}\mathrm{CO_2H}\\ \mathrm{CH_2.CH_2}\end{cases}\\ \qquad\quad |\qquad\qquad\ |\\ \qquad\quad \mathrm{O}\text{———}\mathrm{CO.}\end{array}$$

The latter is produced when isocaprolactone (p. 364) is oxidized with nitric acid (*Annalen* 208, 62), and by the action of CNK and hydrochloric acid upon lævulinic acid (p. 343). It yields deliquescent needles, melting at 68–70°. Salts of methyl glutaric acid are formed when it is boiled with bases.

5. Acids, $\mathrm{C_7H_{12}O_5}$.

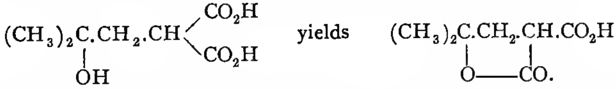
(1) **Ethyl Itamalic Acid,** $\mathrm{C_7H_{12}O_5}$, and **Ethyl Paraconic Acid,** $\mathrm{C_7H_{10}O_4}$:—



$$\mathrm{C_2H_5.CH(OH).CH}\begin{cases}\mathrm{CO_2H}\\ \mathrm{CH_2.CO_2H}\end{cases}\quad\text{yields}\quad\begin{array}{l}\mathrm{C_2H_5.CH.CH}\begin{cases}\mathrm{CO_2H}\\ \mathrm{CH_2.}\end{cases}\\ \qquad\qquad |\qquad\qquad\ |\\ \qquad\qquad \mathrm{O}\text{———}\mathrm{CO}\end{array}$$

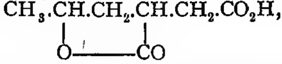
β-Caprolactonic acid is obtained from propionic aldehyde and sodium succinate (p. 463), and crystallizes in needles or leaflets, melting at 85° C. If boiled with bases it forms salts of ethylparaconic acid with the formula $\mathrm{C_7H_{10}O_5M\acute{e}_2}$. When distilled it breaks up chiefly into carbon dioxide and caprolactone (p. 364). Isomeric hydrosorbic acid is formed at the same time (p. 245) (*Berichte*, 23, Ref. 93).

(2) **Diaterebic Acid,** $\mathrm{C_7H_{12}O_5}$, and **Terebic Acid,** $\mathrm{C_7H_{10}O_4}$:—



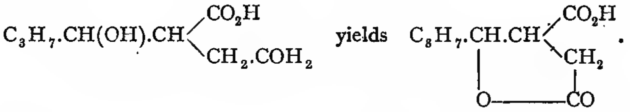
$$\begin{array}{l}\mathrm{(CH_3)_2C.CH_2.CH}\begin{cases}\mathrm{CO_2H}\\ \mathrm{CO_2H}\end{cases}\\ \qquad\quad\ |\\ \qquad\quad \mathrm{OH}\end{array}\quad\text{yields}\quad\begin{array}{l}\mathrm{(CH_3)_2C.CH_2.CH.CO_2H}\\ \qquad\quad\ |\qquad\quad\ |\\ \qquad\quad \mathrm{O}\text{——}\mathrm{CO.}\end{array}$$

Terebic acid is formed when turpentine oil is oxidized with nitric acid (also some dimethyl fumaric acid, p. 430) and when teraconic acid (p. 431) is heated with hydrobromic or sulphuric acid (p. 352). It is sparingly soluble in cold water, crystallizes in shining prisms, melts at 175° and sublimes even below this temperature. It is a monobasic acid, and with carbonates yields the salts $\mathrm{C_7H_9MeO_4}$, which are generally easily soluble ; stronger bases will change these compounds into salts of dibasic-diaterebic acid, $\mathrm{C_7H_{10}Me_2O_5}$. When terebic acid is distilled it forms carbon dioxide and pyroterebic acid (isocaprolactone is produced at the same time, p. 364). When sodium acts on the ethyl salt it forms ethyl teraconate (431) (*Annalen*, 226, 363).

(3) **Carbocaprolactonic Acid,**  $CH_3.CH.CH_2.CH.CH_2.CO_2H$ (O—CO bridge), from allyl succinic acid (p. 430), melts at 69°, and distils with scarcely any decomposition at 260°.

6. Acids, $C_8H_{14}O_5$.

(1) **Propylitamalic Acid,** $C_8H_{14}O_5$, and **Propylparaconic Acid,** $C_8H_{12}O_4$:—



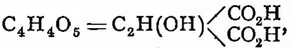
$$C_3H_7.CH(OH).CH\langle{}^{CO_2H}_{CH_2.COH_2} \quad \text{yields} \quad C_3H_7.CH.CH\langle{}^{CO_2H}_{CH_2} \text{ (O—CO ring)}.$$

Propylparaconic acid is obtained from butyraldehyde and succinic acid. It melts at 73.5°. On boiling with bases it forms salts of propylitamalic acid, $C_8H_{12}O_5Me_2$. Heptolactone, heptylenic acid, $C_7H_{12}O_2$, and propylitaconic acid, $C_8H_{12}O_4$ (*Berichte*, 20, 3180), are produced by the distillation of propylparaconic acid.

(2) **Isopropylitamalic and Isopropylparaconic Acids** are similarly obtained from isobutyraldehyde and succinic acid. The second melts at 69°, and when distilled decomposes into isoheptolactone and isoheptylenic acid (*Berichte*, 23, Ref. 94).

(3) **Diaterpenylic Acid,** $C_8H_{14}O_5$. Its lactone, **Terpenylic Acid,** $C_8H_{12}O_4$, is obtained by oxidizing turpentine oil and various terpenes with potassium chlorate and sulphuric acid (*Berichte*, 18, 3207). It crystallizes in large leaflets with one molecule of water, and melts when anhydrous at 90°. It unites with carbonates and forms salts of terpenylic acid, $C_8H_{11}MeO_4$. Caustic alkalies convert these into salts of dibasic diaterpenylic acid, $C_8H_{12}Me_2O_5$. When distilled, terpenylic acid decomposes into carbon dioxide and teracrylic acid, $C_7H_{12}O_2$ (p. 241).

UNSATURATED OXYDICARBOXYLIC ACIDS, $C_nH_{2n-4}O_5$.

The supposed **Oxymaleïc Acid,**  $C_4H_4O_5 = C_2H(OH)\langle{}^{CO_2H}_{CO_2H}$, from brommaleïc acid, appears not to exist (*Annalen*, 227, 233).

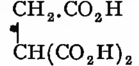
Oxyitaconic Acid, $C_5H_6O_5$, is only stable in its salts. Its lactone acid—monobasic **Aconic Acid,** $C_5H_4O_4$—results from boiling monobromitaconic acid (from itabrompyrotartaric acid, p. 418), with water. Soluble rhombic crystals, melting at 164°. It is not capable of combining with bromine (*Annalen*, 216, 91).

Oxycitraconic Acid, $C_5H_6O_5$, is obtained from chlorcitramalic acid (p. 468) by means of baryta water. It forms readily soluble prisms. It does not unite with bromine or nascent hydrogen, but when heated to 110° with hydriodic acid, it is converted into citramalic acid, $C_5H_8O_5$. When boiled with water, it decomposes into $2CO_2$ and propionic aldehyde (*Annalen*, 227, 237).

Oxyhydromuconic Acid, $C_6H_8O_5$. Its lactone-anhydride, monobasic **Mucolactonic Acid, or Muconic Acid,** $C_6H_6O_4$, is obtained by heating dibromadipic acid, $C_6H_8Br_2O_4$ (from hydromuconic acid, p. 430), with silver oxide. Large, readily soluble crystals, which melt near 100°. It decomposes into carbon dioxide and acetic and succinic acids when boiled with baryta water.

TRIBASIC ACIDS, $C_nH_{2n-4}O_6$.

Formyl Tricarboxylic Acid, Methenyl Tricarboxylic Acid, $CH(CO_2H)_3 = C_4H_4O_6$, is decomposed into carbon dioxide and malonic acid, $CH_2(CO_2H)_2$, when it is freed from its esters by alkalies or acids (p. 401). The *triethyl ester*, $CH(CO_2.C_2H_5)_3$, is obtained from sodium malonic ester, $CHNa(CO_2.C_2H_5)_2$, and ethyl chlorcarbonate (*Berichte*, 21, Ref. 531); it is crystalline, melts at 29°, and boils at 253°. Sodium alcoholate decomposes it.

Ethenyl Tricarboxylic Acid,  $\begin{array}{l} CH_2.CO_2H \\ | \\ CH(CO_2H)_2 \end{array}$ $= C_5H_6O_6$, is obtained by the saponification of ethyl acetylene tetracarboxylate, $C_2H_2(CO_2.C_2H_5)_4$, and from esters of cyansuccinic acid, $C_2H_3(CN)(CO_2R)_2$. It melts at 159° and is decomposed into carbon dioxide and succinic acid. The *ethyl ester*, $C_5H_3(C_2H_5)_3O_6$, is obtained from sodium ethyl malonate and the ester of chloracetic acid. It boils at 278°. Chlorine converts it into **Chlorethenyl Tricarboxylic Ester,** $C_2H_2Cl(CO_2.C_2H_5)_3$. This boils at 290°, and when heated with hydrochloric acid, yields carbon dioxide, hydrochloric acid, alcohol and fumaric acid; when saponified with alkalies, carbon dioxide and malic acid are the products (*Annalen*, 214, 44).

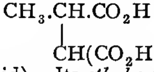
Higher tricarboxylic acids have been variously produced by analogous methods:

(1) By the action of the esters of haloid fatty acids upon the sod-malonic esters, $CHNa.(CO_2R)_2$, and the sod-alkyl-malonic esters, $R.CNa(CO_2R)_2$.

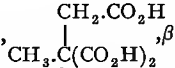
(2) By the action of alkyl haloids upon esters of ethenyl tricarboxylic esters.

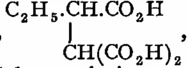
Of the resulting isomeric acids, those obtained by the second method are designated β-derivatives of ethane- or ethenyl-tricarboxylic acid (see above).

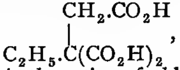
Many tri- and poly-carboxylic acids have been prepared. They lose carbon dioxide, and yield the corresponding mono- and dialkylic succinic acids (p. 400) (*Annalen*, 214, 58; *Berichte*, 16, 333; 23, 633).

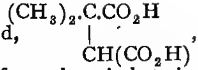
α-Methyl Ethenyl Tricarboxylic Acid, $C_6H_8O_6 =$  $\begin{array}{l} CH_3.CH.CO_2H \\ | \\ CH(CO_2H)_2 \end{array}$, **α-propenyl tricarboxylic acid** (isomeric with tricarballylic acid). Its *ethyl ester*, $C_6H_5O_6(C_2H_5)_3$, is prepared from ethyl malonate and the ester of α-brompropionic acid. It boils at 270°.

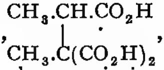
The free acid melts at 140°, and breaks down into carbon dioxide and methyl succinic acid.

β-Methyl Ethenyl Tricarboxylic Acid,  $\begin{array}{l} CH_2.CO_2H \\ | \\ CH_3.C(CO_2H)_2 \end{array}$, **β propenyl tricarboxylic acid.** Its *methyl ester* is formed when chloracetic ester acts upon methyl malonic ester, or methyl iodide upon ethenyl tricarboxylic ester. It boils at 273°. It yields methyl succinic acid when saponified with sulphuric acid.

α-Ethyl Ethenyl Tricarboxylic Acid,  $\begin{array}{l} C_2H_5.CH.CO_2H \\ | \\ CH(CO_2H)_2 \end{array}$, **α-butane tricarboxylic acid.** The ethyl ester is obtained from malonic ester and α-brombutyric ester. It boils at 278°. It passes, by saponification, into ethyl succinic acid.

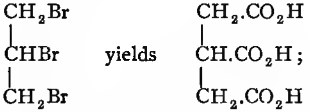
β-Ethyl Ethenyl Tricarboxylic Acid,  $\begin{array}{l} CH_2.CO_2H \\ | \\ C_2H_5.C(CO_2H)_2 \end{array}$, **β-butane tricarboxylic acid.** The ethyl ester is formed in the action of chloracetic ester upon ethyl malonate, as well as that of ethyl iodide upon ethenyl tricarboxylic ester. It boils at 281°. It forms ethyl succinic acid when saponified.

α-Dimethyl Ethenyl Tricarboxylic Acid,  $\begin{array}{l}(CH_3)_2.C.CO_2H\\ \mid\\ CH(CO_2H)\end{array}$, **isobutylene tricarboxylic acid.** Its ethyl ester is obtained from α-bromisobutyric ester, $(CH_3)_2.CBr.CO_2.C_2H_5$, and malonic ester. It boils at 277° C. It yields unsymmetrical dimethyl succinic acid (p. 420) when saponified.

αβ Dimethyl Ethenyl Tricarboxylic Acid,  $\begin{array}{l}CH_3.CH.CO_2H\\ \mid\\ CH_3.C(CO_2H)_2\end{array}$, **butane tricarboxylic acid.** Its ethyl ester is made from α-brompropionic ester and methyl malonic ester, as well as by the action of methyl iodide upon α-propenyl tricarboxylic ester. It boils at 279°, and yields both dimethyl succinic acids (p. 420) when saponified.

αβ-Methyl-ethyl-, αβ-diethyl-, etc., ethenyl tricarboxylic esters, $(RR')C_2H_3(CO_2R)_3$, have been produced in an analogous manner. They have also yielded the corresponding alkylic succinic acids when saponified (p. 400 and *Berichte*, **23**, 647).

Tricarballylic Acid, $C_6H_8O_6 = C_3H_5(CO_2H)_3$, is obtained: (1) by heating tribromallyl with potassium cyanide and decomposing the tricyanide with potash :—



$$\begin{array}{lcl}CH_2Br & & CH_2.CO_2H\\ \mid & & \mid\\ CHBr & \text{yields} & CH.CO_2H;\\ \mid & & \mid\\ CH_2Br & & CH_2.CO_2H\end{array}$$

(2) by oxidizing diallyl acetic acid (p. 245); (3) by acting upon ethyl aceto-succinate with sodium and the ester of chloracetic acid, then saponifying the aceto-tricarballylic ester (p. 342); (4) by the decomposition of α-propylene-tetracarboxylic acid; (5) by the action of nascent hydrogen upon aconitic acid, $C_6H_6O_6$ (*Berichte*, **22**, 2921), and by the reduction of citric acid with hydriodic acid; also from dichlorglycide, $C_3H_4Cl_2$, and chlorcrotonic ester, $C_4H_4ClO_2.C_2H_5$, by the action of potassium cyanide. The acid occurs in unripe beets, and also in the deposit in the vacuum pans used in beet-sugar works. It crystallizes in rhombic prisms, which dissolve easily in water, alcohol and ether, and melt at 158° (166°).

The *silver salt*, $C_6H_5O_6Ag_3$, is insoluble in water. *Calcium tricarballylate* $(C_6H_5O_6)_2Ca_3 + 4H_2O$, is a powder that dissolves with difficulty. The *trimethyl ester*, $C_6H_5O_6(CH_3)_3$, boils at 150°, under a pressure of 13 mm. The *chloride* of tricarballylic acid, $C_3H_5(CO.Cl)_3$, results from the action of phosphorus pentachloride. The *triamide*, $C_3H_5(CO.NH_2)_3$, melts at 206°.

Aconitic Acid, $C_6H_6O_6 = C_3H_3(CO_2H)_3$* belongs to the class of unsaturated tricarboxylic acids.

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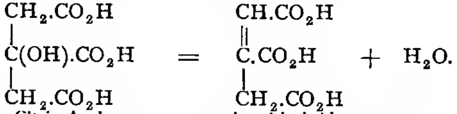
* It is isomeric with trimethylene tricarboxylic acid (see this).

It occurs in different plants, for example, in *Aconitum Napellus*, in *Equisetum fluviatile*, in sugar cane and in beet roots. It is obtained by heating citric acid alone or with concentrated hydrochloric acid:—



$$\begin{array}{l} CH_2.CO_2H \\ | \\ C(OH).CO_2H \\ | \\ CH_2.CO_2H \end{array} = \begin{array}{l} CH.CO_2H \\ \| \\ C.CO_2H \\ | \\ CH_2.CO_2H \end{array} + H_2O.$$

Citric Acid. Aconitic Acid.

Its formation, when acetylene dicarboxylic acid is treated with alcoholic potash, is rather peculiar (*Berichte*, 22, 3055).

Preparation.—Citric acid is rapidly heated in a flask until the formation of white vapors ceases and oily streaks line the neck. The residue is taken up in a little water, evaporated to crystallization, and the crystalline deposit extracted with ether, which will dissolve only aconitic acid. To obtain the latter pure, decompose the lead salt with hydrogen sulphide (*Berichte*, 9, 1751).

A better method consists in boiling citric acid (100 grs.) with water (50 grs.) and sulphuric acid (100 grs.) for a period of 4–6 hours (*Berichte*, 20, Ref. 254).

Aconitic acid crystallizes in small plates, which dissolve readily in alcohol, ether and water. It melts at 186–187° and decomposes into carbon dioxide and itaconic acid. Nascent hydrogen converts it into tricarballylic acid, $C_6H_6O_6 + H_2 = C_6H_8O_6$.

It gives rise to three series of salts. The tertiary *lead salt* is insoluble in hot water. The *calcium salt* $(C_6H_3O_6)_2Ca_3 + 6H_2O$, dissolves with difficulty. The esters of aconitic acid are obtained by conducting hydrochloric acid gas into alcoholic solutions of the acid (*Berichte*, 21, 670); as well as by heating aceto-citric esters to 250–280°. The *trimethyl ester*, $C_6H_3O_6(CH_3)_3$, is a yellow oil. It boils at 200°.

Concentrated ammonia converts the esters into *aconitic triamide*, $C_3H_3(CO.NH_2)_3$. A yellow, crystalline powder, soluble in water. Acids change it to citrazic acid (= dioxypyridine carboxylic acid) (*Berichte*, 22, 1078, 3054; 23, 831).

Isomeric *Pseudo-aconitic Acid*, $C_6H_6O_6$, results upon heating *a*-propylene tetracarboxylic acid (p. 482) to 200°, when it splits off carbon dioxide. It melts at 145–150° C.

TETRAVALENT COMPOUNDS.

TETRAHYDRIC ALCOHOLS.

Ortho-carbonic Ester, $C(O.C_2H_5)_4$ (of Basset), may be regarded as the ether ot the tetrahydric alcohol or normal carbonic acid, $C(OH)_4$. It is produced when sodium ethylate acts on chloropicrin:—

$$CCl_3(NO_2) + 4C_2H_5.ONa. = C(O.C_2H_5)_4 + 3NaCl + NO_2Na.$$

It is a liquid with an ethereal odor, and boils at 158–159°. When heated with ammonia it yields guanidine.

The *propyl ester*, $C(O.C_3H_7)_4$, boils at 224, the *isobutyl ester* at 250°, and it seems the *methyl ester* cannot be prepared (*Annalen*, 205, 254).

Erythrol, Erythrite, $C_4H_{10}O_4 = CH_2(OH).CH(OH).CH(OH).CH_2.OH$, **Erythroglucin** or **Phycite,** occurs free in the alga *Protococcus vulgaris.* It exists as erythrin (orsellinate of erythrite) in many lichens and some algæ, especially in *Roccella Montagnei*, and is obtained from these by saponification with caustic soda or milk of lime:—

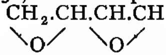
$$\underset{\text{Erythrin.}}{C_4H_6\left\{\begin{matrix}(OH)_2\\(O.C_8H_7O_3)_2\end{matrix}\right.} + 2H_2O = \underset{\text{Erythrol.}}{C_4H_6(OH)_4} + \underset{\text{Orsellinic Acid.}}{2C_8H_8O_4}.$$

Erythrol forms large quadratic crystals, which dissolve readily in water, with difficulty in alcohol, and are insoluble in ether. Like all polyhydric alcohols erythrol possesses a sweet taste. It melts at 126° and boils at 330° (*Berichte*, 17, 873). When heated with hydriodic acid it is reduced to secondary butyl iodide:—

$$C_4H_6(OH)_4 + 7HI = C_4H_9I + 4H_2O + 3I_2.$$

By carefully oxidizing erythrol with dilute nitric acid an *aldehyde body* is obtained, which combines with two molecules of phenylhydrazine to form phenyl erythrosazone, $C_4H_6O_2(N_2H.C_6H_5)_2$, melting at 167° (*Berichte*, 20, 1090). More intense oxidation with nitric acid produces inactive tartaric acid.

Erythrol yields esters with acids. The nitric acid ester, the so-called *nitroerythrite*, $C_4H_6(O.NO_2)_4$, is obtained by dissolving erythrol in fuming nitric acid; it separates in brilliant plates, melting at 61°. It burns with a bright flame and explodes violently when struck.

Concentrated hydrochloric acid converts *Erythrol* into the dichlorhydrin, $C_4H_6(OH)_2Cl_2$ (melting at 125°). Caustic potash converts this into the dioxide, the so-called *Erythrol ether*,  $\underbrace{CH_2.CH}_{O}.\underbrace{CH.CH_2}_{O}$. This is a pungent-smelling liquid of sp. gr. 1.113 at 18°; boils at 138° and volatilizes with ether vapors. In its reactions it is perfectly similar to the alkylen oxides (p. 300). It combines gradually with water, forming erythrol, with 2HCl yielding dichlorhydrin, with 2CNH to form the nitrile of dioxyadipic acid, etc. (*Berichte*, 17, 1091).

MONOBASIC ACIDS.

Erythritic Acid, $C_4H_8O_5 = C_3H_4\left\{\begin{matrix}(OH)_3\\CO_2H\end{matrix}\right.$, erythroglucic acid, trioxybutyric acid, is produced in the oxidation of an aqueous erythrol solution with platinum sponge. It forms a deliquescent crystalline mass. The same acid is probably formed on oxidizing lævulose with mercuric oxide or bromine water (*Berichte*, 19, 390). It also results from the oxidation of mannitol with potassium permanganate (*Berichte*, 19, 468).

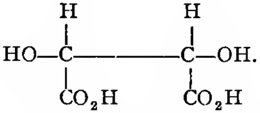
DIBASIC ACIDS.

Dioxymalonic Acid, $C_3H_4O_6 = C(OH)_2 \begin{array}{l} \diagup CO_2H \\ \diagdown CO_2H \end{array}$, obtained from dibrommalonic acid, is identical with mesoxalic acid (p. 434).

Tartaric Acid, $C_4H_6O_6 = \begin{array}{l} CH(OH)—CO_2H \\ | \\ CH(OH)—CO_2H \end{array}$, or **Dioxysuccinic Acid.**

Several modifications of this acid are known; all possess the same structure (*Berichte*, 21, 519) and can be converted into each other. They are the ordinary or dextro-tartaric acid, lævo-tartaric acid, racemic acid and inactive mesotartaric acid. They are chiefly distinguished by their different optical rotatory power, but all, however, yield the same products of transposition, hence they are viewed as physical isomerides (p. 49).

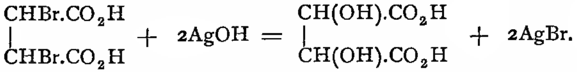
The differences in these acids, according to the Le Bel-van't Hoff theory, are attributable to the presence of two *asymmetric* carbon atoms in dioxysuccinic acid (p. 63):—



$$\begin{array}{ccccc} & H & & H & \\ & | & & | & \\ HO— & C & ———— & C & —OH. \\ & | & & | & \\ & CO_2H & & CO_2H & \end{array}$$

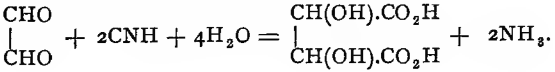
The two intermediate carbon tetrahedra, having a common axis and joined by one summit, have the three different groups arranged right or left. This would result in a dextro- and lævo-rotatory tartaric acid. If, however, the three side groups are arranged in opposite directions, their influence will cease, and the product will be an *inactive* tartaric acid. This cannot be resolved; it is known as the *meso-* or *anti-*form. Again, the dextro- and lævo-modifications can unite, producing an optically *inactive* modification, that can be resolved into its two active components. This is the *para*-form. It is represented by racemic acid (p. 478). Consequently, dioxysuccinic acid can exist according to theory in three or four different modifications. This is confirmed, too, by many facts (*Berichte*, 21, 2106; 22, 1813).

Dioxysuccinic acid is synthetically prepared by boiling dibromsuccinic acid with moist silver oxide:—



$$\begin{array}{l} CHBr.CO_2H \\ | \\ CHBr.CO_2H \end{array} + 2AgOH = \begin{array}{l} CH(OH).CO_2H \\ | \\ CH(OH).CO_2H \end{array} + 2AgBr.$$

The product in this reaction consists of inactive tartaric acid and racemic acid. Only the latter is formed when hydrocyanic acid and hydrochloric acid (p. 324) act upon glyoxal:—



$$\begin{array}{l} CHO \\ | \\ CHO \end{array} + 2CNH + 4H_2O = \begin{array}{l} CH(OH).CO_2H \\ | \\ CH(OH).CO_2H \end{array} + 2NH_3.$$

Racemic acid is also produced when fumaric acid is oxidized with potassium permanganate, while maleïc acid, by the same treatment, yields inactive tartaric acid. Mannitol, when oxidized with nitric acid, yields racemic acid, and sorbine yields inactive tartaric acid.

Racemic acid can yield dextro- and lævo-tartaric acid (p. 478). Heat converts ordinary dextro-tartaric acid and also racemic acid into inactive tartaric acid; conversely, the latter can change to racemic acid by heat (p. 478).

All the tartaric acids, when heated with hydriodic acid, sustain a reduction of the OH-groups and change first to malic and then into succinic acid (p. 410); in this case active tartaric acid yields malic acid, the inactive tartaric, however, inactive malic acid—whereas succinic acid is always inactive (p. 64).

1. **Dextro-rotatory or Ordinary Tartaric Acid** (*Acidum tartaricum*) is widely distributed in the vegetable world, and occurs principally in the juice of the grape, from which it deposits after fermentation in the form of acid potassium tartrate (argol). It results on oxidizing saccharic acid and milk sugar with nitric acid.

Preparation.—Crude argol is purified by crystallization and boiled with pulverized chalk and water; this causes it to separate into easily soluble, neutral potassium tartrate and neutral calcium tartrate, which separates as an insoluble powder. Calcium chloride precipitates all the tartaric acid as neutral calcium salt from the filtered solution containing neutral potassium tartrate. The calcium salt is decomposed by dilute sulphuric acid, the gypsum filtered off, and the solution concentrated by evaporation.

Common tartaric acid crystallizes in large monoclinic prisms, which dissolve readily in water and alcohol, but not in ether. Its solution turns the ray of polarized light to the right. It melts at 167–170° (*Berichte*, **22**, 1814), when rapidly heated, and in so doing is converted into an amorphous modification, called *metatartaric acid*, which crystallizes again from water as tartaric acid. Heated for some time at 150° water escapes, and we get the anhydrides (p. 351): Ditartaric acid (or tartralic acid), $C_8H_{10}O_{11}$, *tartrelic acid* and *tartaric anhydride*, $C_4H_4O_5$. The latter is a white powder which reverts to tartaric acid when boiled with water. Pyroracemic and pyrotartaric acids are products of its dry distillation.

When gradually oxidized tartaric acid becomes oxymalonic acid (p. 463); stronger oxidizing agents decompose it into carbon dioxide and formic acid.

Tartrates.—The acid forms salts which contain usually one and two equivalents of metal; there are, however, some with four equivalents of metal; here four hydrogen atoms (two of the CO_2H groups and two of the OH groups) are replaced. The polyvalent acids form such salts with less basic metals, like lead and tin.

The *neutral potassium salt*, $C_4H_4K_2O_6 + \frac{1}{2}H_2O$, is readily soluble in water; from it acids precipitate the salt $C_4H_5KO_6$, which is not very soluble in water, and constitutes natural tartar (*Cremor tartari*).

Potassium-Sodium Tartrate, $C_4H_4KNaO_6 + 4H_2O$ (*Seignette's salt*), is made by saturating cream of tartar with a sodium-carbonate solution. It crystallizes in large prisms with hemihedral faces. The *calcium salt*, $C_4H_4CaO_6 + 4H_2O$, is precipitated from solutions of neutral tartrates, by calcium chloride, as an insoluble, crystalline powder. It dissolves in acids and alkalies, and is reprecipitated on boiling—a reaction serving to distinguish tartaric from other acids. Consult *Annalen*, 226, 161, upon the calcium salts of the different tartaric acids.

The *neutral lead salt*, $C_4H_4PbO_6$, is a curdy precipitate. On boiling its ammonia solution a basic salt, $C_4H_2Pb_2O_6$, is deposited; in this the hydrogen atoms of the four OH groups of tartaric acid are replaced by lead.

Potassio-antimonious Tartrate, $C_4H_4(SbO)KO_6 + \frac{1}{2}H_2O$, tartar emetic. In this an atom of hydrogen is replaced by antimonyl (SbO) (*Berichte*, 13, 1787). It is prepared by boiling cream of tartar with antimony oxide and water. It crystallizes in rhombic octahedrons, which slowly lose their water of crystallization on exposure and fall to a powder. It is soluble in 14 parts water at 10°. Its solution possesses an unpleasant, metallic taste, and acts as a sudorific and emetic. When the salt is heated to 200°, 1 molecule of water escapes and we get the basic salt, $C_4H_2\overset{///}{Sb}KO_6$, corresponding to basic lead tartrate. Consult *Berichte*, 16, 2379.

To obtain the esters of tartaric acid, $C_2H_4O_2(CO_2R)_2$, dissolve the acid in methyl or ethyl alcohol, conduct hydrochloric-acid gas through the solution, and distil the liquid under diminished pressure, repeating the process (*Berichte*, 13, 1175). The esters of the other tartaric acids are similarly obtained (*Berichte*, 18, 1397). The *dimethyl ester*, $C_4H_4O_6(CH_3)_2$, is crystalline, melts at 48°, and boils at 280°. The *diethyl ester*, $C_4H_4O_6(C_2H_5)_2$, is a liquid, also boiling at 280°. It is dextrorotatory. The *dipropyl ester*, boils at 300° C.

When acetyl chloride acts upon the diethyl ester, the hydrogen of the alcoholic hydroxyl groups is replaced and we obtain acetyl and diethyl diacetyl tartaric esters, $C_2H_2(O.C_2H_3O)_2(CO_2.C_2H_5)_2$; the first is a liquid; the second melts at 67°, and boils without decomposition at 290°.

The nitro-group, NO_2, can effect the same kind of substitution as noted above (p. 302). By dissolving pulverized tartaric acid in concentrated nitric acid and adding sulphuric acid, so-called *Nitro-tartaric Acid*, $C_2H_2(O.NO_2)_2\left\langle\begin{matrix}CO_2H\\CO_2H\end{matrix}\right.$, results. This is a gummy mass, which on drying becomes white and shining. It is soluble in water. When its solution is heated tartronic acid is produced. It slowly decomposes into tetra-oxysuccinic acid.

Tartramic Acid, $C_2H_2(OH)_2\left\langle\begin{matrix}CO.NH_2\\CO_2H\end{matrix}\right.$. Its ammonium salt is obtained by acting on tartaric anhydride, $C_4H_4O_5$, with ammonia. From a solution of this salt calcium chloride precipitates calcium tartramate. The acid can be obtained in large crystals from the latter.

Tartramide, $C_2H_2(OH)_2\left\langle\begin{matrix}CO.NH_2\\CO.NH_2\end{matrix}\right.$, is produced by the action of ammonia upon diethyl tartrate.

2. *Lævo-Tartaric Acid* is very similar to the dextro-variety, also melts at 167–170°, and only differs from it in deviating the ray of polarized light to the left. Their salts are very similar, and usually isomorphous, but those of the lævo-acid exhibit opposite hemihedral faces. On mixing the two acids, we get the optically inactive racemic acid, which in turn may be separated into the two original acids (see below).

The *esters* of lævo-tartaric acid are obtained in the same manner as those of the dextro-acid (see above). The *dimethyl ester*, $C_4H_4O_6(CH_3)_2$, is similar to that of the latter. It melts at 48°, and boils at the same temperature as the dextro-ester. It is, however, lævo-rotatory.

3. *Racemic Acid* is sometimes found in conjunction with tartaric acid in the juice of the grape, and is obtained from the mother liquor in crystallizing cream of tartar.

The mother liquor is boiled and saturated with chalk; the calcium salt which separates is decomposed with sulphuric acid and the filtrate evaporated to crystallization. As the crystals of racemic acid effloresce on exposure to the air, they can be readily separated mechanically from ordinary tartaric acid.

Racemic acid appears in the oxidation of mannitol, dulcitol and mucic acid with nitric acid. It is synthetically obtained from glyoxal by means of prussic and hydrochloric acids, and (together with meso-tartaric acid) from dibromsuccinic acid, by the action of silver oxide (p. 475); in addition by heating desoxalic acid or its ester (p. 485) with water or dilute acids to 100°:—$C_5H_6O_8 = C_4H_6O_6 + CO_2$. An interesting method of preparing it is that of oxidizing fumaric acid with potassium permanganate (p. 426).

Racemic acid is most readily made by heating ordinary tartaric acid with water ($\frac{1}{10}$ part) to 175°. The product consists of inactive tartaric acid and racemic acid. These can be separated very easily by crystallization.

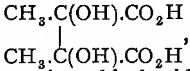
Racemic acid crystallizes in prisms having a molecule of water. These slowly effloresce in dry air, and at 100° lose water. It is less soluble (1 part in 5.8 parts at 15°) in water than the tartaric acid, and has no effect on polarized light. It loses its crystal water when heated to 110°. In the anhydrous condition it melts at 205–206°. It foams at the same time. Its salts closely resemble those of tartaric acid, but do not show hemihedral faces. The acid potassium salt is appreciably more soluble than cream of tartar. The calcium salt dissolves with more difficulty, and is even precipitated by the acid from solutions of calcium chloride and gypsum. Acetic acid and ammonium chloride do not dissolve it.

The acid is composed of dextro- and lævo-tartaric acids. It is most readily converted into these through the sodium ammonium salt, $C_4H_4Na(NH_4)O_6 + 4H_2O$. On saturating acid sodium racemate with ammonia and allowing it to crystallize, large rhombic crystals form. Some of these show right, others left hemihedral faces. Removing the similar forms, we discover that the former possess right-rotatory power and yield common tartaric acid, whereas the latter yield the lævo-acid. The separation is easier if we project crystal fragments into a supersaturated mixture of the acids. In this case only crystals of the forms introduced will separate. By mixing dextro- and lævo-acid, we again obtain racemic acid. Penicillium glaucum destroys the dextro-tartaric acid, and thus decomposes the racemic acid.

The methods employed for the preparation of the esters of ordinary tartaric acid (p. 477) will serve for the production of those of racemic acid. The *dimethyl ester*, $C_4H_4O_6(CH_3)_2$, consisting of monoclinic prisms, melts at 85° and boils at 282°. It is inactive. It can be made with exactly the same properties by fusing together the dimethyl ester of dextro- and lævo-tartaric acids. In vapor form the ester of racemic acid has the simple formula given above; hence, in this condition it consists of the dimethyl ester of the dextro- and lævo-tartaric acids, and upon cooling these reunite to the dimethyl ester of racemic acid (*Berichte*, 18, 1397). The dimethyl-diethyl racemic ester deports itself similarly (*Berichte*, 21, Ref. 643.)

4. *Inactive Tartaric Acid, Mesotartaric Acid, Antitartaric Acid*, is obtained when sorbine and erythrol are oxidized with nitric acid, or when dibromsuccinic acid is treated with silver oxide (p. 475) and maleïc acid with potassium permanganate (p. 426). It is most readily prepared by heating common tartaric acid with water to 65° for two days. The acid potassium salt affords a means of separating it from unaltered acid and the little racemic acid produced at the same time. At 175° more racemic acid is obtained. The latter acid, when heated alone or with water to 170–180°, may be changed to the inactive acid. Conversely, when the inactive acid is raised to the same temperature with water, it is transformed into racemic acid; a state of equilibrium occurs between the two acids in solution; this can be overcome by removing one of the acids and by repeated heatings (Jungfleisch).

Mesotartaric acid resembles racemic acid very much. It is more soluble in water (1 part in 0.8 parts at 15°). It crystallizes in long prisms containing one molecule of water. These effloresce in the dessicator, lose all their water at 110°, and then melt at 143°. The acid is optically inactive and cannot be directly transformed into the active tartaric acids. Its salts and esters also distinguish it from racemic acid (*Berichte*, 17, 1412; 21, 519).



Dimethyl Racemic Acid, $C_6H_{10}O_6 = \begin{array}{l} CH_3.C(OH).CO_2H \\ \quad | \\ CH_3.C(OH).CO_2H \end{array}$, is a homologue of racemic acid. It is produced when hydrocyanic and hydrochloric acids act upon diacetyl, $CH_3.CO.CO.CH_3$ (p. 326). This procedure is analogous to that by which glyoxal yields racemic acid. The acid contains one molecule of crystal water and when anhydrous, melts at 179° (*Berichte*, 22, Ref. 137).

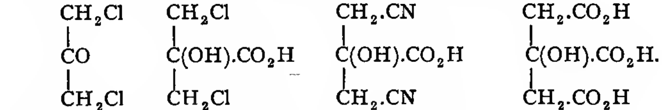
TRIBASIC ACIDS.

The supposed *Carboxytartronic Acid*, $C_4H_4O_7 = C(OH)(CO_2H)_3$, has been proved to be a dibasic acid — *Tetraoxysuccinic Acid*, $C_2(OH)_4.(CO_2H)_2 = C_4H_6O_8$ (p. 491).

Citric Acid, $C_6H_8O_7 = C_3H_4(OH)(CO_2H)_3$, oxytricarballylic acid (*Acidum citricum*), occurs free in lemons, in black currants, in bilberry, in beets and in other acid fruits. It is obtained from lemon juice for commercial purposes.

Lemon juice is boiled (to coagulate albuminoid substances), filtered and saturated with calcium carbonate and slacked lime. The calcium salt which separates is decomposed with sulphuric acid and the filtrate concentrated.

The acid can be prepared synthetically from β-dichloracetone; this is accomplished by first acting on the latter compound with prussic acid and hydrochloric acid, when we get dichloroxyisobutyric acid (p. 363), which is then treated with KCN and a cyanide obtained. The latter is saponified with hydrochloric acid:—



$$\begin{array}{llll} CH_2Cl & CH_2Cl & CH_2.CN & CH_2.CO_2H \\ | & | & | & | \\ CO & C(OH).CO_2H & C(OH).CO_2H & C(OH).CO_2H. \\ | & | & | & | \\ CH_2Cl & CH_2Cl & CH_2.CN & CH_2.CO_2H \end{array}$$

β-Dichloracetone. Dichloroxyisobutyric Acid. Dicyanoxyisobutyric Acid. Citric Acid.

Citric acid is also obtained by the action of prussic and hydrochloric acids upon acetone dicarboxylic acid, and from cyanacetic ester, $CN.CH_2.CO.CH_2.CO_2R$, by the same reagents (*Berichte*, **22**, Ref. 256).

Citric acid crystallizes with one molecule of water in large rhombic prisms, which melt at 100°, lose their crystal water at 130° and then melt at 153°. It dissolves in 4 parts of water of ordinary temperatures, readily in alcohol and with difficulty in ether. The aqueous solution is not precipitated by milk of lime when cold, but on boiling the tertiary calcium salt separates. This is insoluble, even in potash (see Tartaric Acid). When heated to 175° citric acid decomposes into water and aconitic acid (p. 472). It breaks up into acetic and oxalic acids when fused with caustic potash, and by oxidation with nitric acid. Acetone dicarboxylic acid (p. 435) is produced when citric acid is digested with concentrated sulphuric acid.

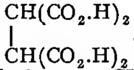
Being a tribasic acid it forms three series of salts. Tertiary potassium citrate, $C_6H_5K_3O_7 + H_2O$, is made by saturating the acid; it consists of deliquescent needles. The secondary salt, $C_6H_6K_2O_7$, is amorphous; the primary salt, $C_6H_7KO_7 + 2H_2O$, forms large prisms. All three dissolve readily in water. Tertiary calcium citrate, $(C_8H_5O_7)_2Ca_3 + 4H_2O$ (p. 480), is a crystalline powder. The *silver salt*, $C_6H_5Ag_3O_7$, is a white precipitate which turns black on exposure.

The neutral esters are produced by conducting hydrochloric acid into hot alcoholic solutions of the acid. The *trimethyl ester*, $C_3H_4(OH).(CO_2.CH_3)_3$, is crystalline, melts at 79° and distils near 285°, decomposing partially at the same time into aconitic ester and water (*Berichte*, **17**, 2683). The *triethyl ester*, $C_3H_4(OH).(CO_2.C_2H_5)_3$, boils near 280° (*Berichte*, **13**, 1953).

The action of acetyl chloride on the esters replaces the alcoholic hydrogen. The *aceto-compound*, $C_3H_4(O.C_2H_5O)(CO_2.C_2H_5)_3$, boils at 280°. It breaks down into acetic acid and aconitic ester, when it is distilled. Nitric acid, too, substitutes the nitro-group for the hydrogen of hydroxyl in the esters.

Citramide, $C_3H_4(OH)(CO.NH_2)_3$, is formed by the action of NH_3 upon ethyl citrate. The mono- and diamine acids are formed at the same time (*Berichte*, **17**, 2682). Citramide is crystalline, dissolves readily in hot water and blackens when heated above 200° C. When digested with hydrochloric or sulphuric acid it is condensed to *citrazinic acid* (dioxypyridine carboxylic acid) (*Berichte*, **23**, 831).

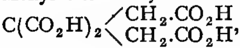
TETRABASIC ACIDS.

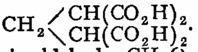
Acetylene Tetracarboxylic Acid,  $\begin{array}{l} CH(CO_2.H)_2 \\ | \\ CH(CO_2.H)_2 \end{array}$. Its ester, $C_6H_2(C_2H_5)_4O_8$, is obtained from sodium malonic ester, $CHNa(CO_2.C_2H_5)_2$, by the action of chlormalonic ester, $CHCl(CO_2.C_2H_5)_2$, or from sodium malonic ester and iodine (*Berichte*, **17**, 2781). It consists of long, shining needles, which melt at 76° and boil at 305°. Aqueous potash converts it into ethenyl tricarboxylic acid and CO_2 (p. 471).

Acetylene tetracarboxylic ester and sodium ethylate yield a disodium compound which unites with o-xylylene bromide, $C_5H_4(CH_2Br)_2$, to form tetrahydronaphthalene tetracarboxylic ester (*Berichte*, **17**, 449).

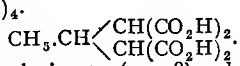
See *Berichte*, **21**, 2085, upon diethyl-ethenyl tetracarboxylic acid.

Acids, $C_7H_8O_8 = C_3H_4(CO_2H)_4$.

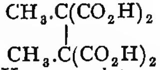
Sodium and ethyl chloracetate change ethenyl tricarboxylic ester into the ester of **α-Propane-Tetracarboxylic Acid**,  $C(CO_2H)_2\begin{array}{l} \diagup CH_2.CO_2H \\ \diagdown CH_2.CO_2H \end{array}$, which boils with slight decomposition at 295°. The free acid is obtained by saponifying the ester. It melts at 151° and decomposes into carbon dioxide and tricarballylic acid.

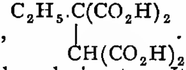
β-Propane Tetracarboxylic Acid,  $CH_2\begin{array}{l} \diagup CH(CO_2H)_2 \\ \diagdown CH(CO_2H)_2 \end{array}$. Its tetraethyl ester is obtained by the condensation of formic aldehyde, CH_2O, or methylene iodide (*Berichte*, **22**, 3294) with two molecules of malonic ester, and by the action of zinc dust and acetic acid upon β-propylene tetracarboxylic acid (*Berichte*, **23**, Ref. 240). It is a thick oil, boiling at 240° under 100 mm. pressure. The free acid decomposes into $2CO_2$ and glutaric acid, $CH_2.(CH_2.CO_2H)_2$ (p. 417). Its disodium compound and alkyl iodides yield dialkyl derivatives. Bromine converts it into β trimethylene tetracarboxylic ester.

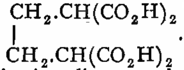
Acids, $C_8H_{10}O_8 = C_4H_6(CO_2H)_4$.

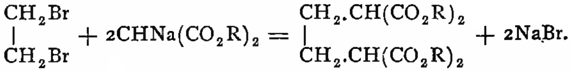
(1) **Ethidene Dimalonic Acid**,  $CH_3.CH\begin{array}{l} \diagup CH(CO_2H)_2 \\ \diagdown CH(CO_2H)_2 \end{array}$. Its ethyl ester is produced by the union of ethidene malonic ester (p. 428) and malonic ester. It

is a thick oil, boiling at 210° under 20 mm. pressure. The free acid separates into $2CO_2$ and ethidene diacetic acid (p. 420) when distilled.

(2) **Dimethyl-Acetylene Tetracarboxylic Acid,**  $\begin{array}{l} CH_3.C(CO_2H)_2 \\ | \\ CH_3.C(CO_2H)_2 \end{array}$. The tetraethyl ester is produced by the introduction of 2 CH_3-groups into acetylene tetracarboxylic ester; also from sodium-methyl malonic ester, $CH_3.CNa(CO_2R)_2$, by the action of iodine (*Berichte*, 18, 1202). The free acid splits off CO_2 and yields symmetrical dimethyl succinic acid (p. 420).

(3) **Ethyl-Acetylene Tetracarboxylic Ester,**  $\begin{array}{l} C_2H_5.C(CO_2H)_2 \\ | \\ CH(CO_2H)_2 \end{array}$. Its ethyl ester is obtained from ethyl malonic ester and chlormalonic ester. It is a thick oil (*Berichte*, 17, 2785).

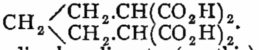
(4) **Butane Tetracarboxylic Acid,**  $\begin{array}{l} CH_2.CH(CO_2H)_2 \\ | \\ CH_2.CH(CO_2H)_2 \end{array}$. The methyl ester is formed together with α-trimethylene dicarboxylic ester when ethylene bromide acts upon sodium malonic ester (*Berichte*, 19, 2038):



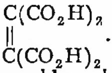
$$\begin{array}{l} CH_2Br \\ | \\ CH_2Br \end{array} + 2CHNa(CO_2R)_2 = \begin{array}{l} CH_2.CH(CO_2R)_2 \\ | \\ CH_2.CH(CO_2R)_2 \end{array} + 2NaBr.$$

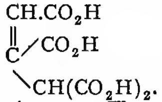
Tetramethylene tetracarboxylic ester is produced when bromine acts upon its disodium compound.

Acids, $C_9H_{12}O_8$.

Pentane-Tetracarboxylic Acid,  $CH_2\begin{array}{l} \diagup CH_2.CH(CO_2H)_2 \\ \diagdown CH_2.CH(CO_2H)_2 \end{array}$. The ethyl ester is formed, together with tetramethylene dicarboxylic ester (see this) in the action of trimethylene bromide upon two molecules of sodium malonic ester (*Berichte*, 18, 3249). Its disodium compound, when acted upon by bromine, yields pentamethylene-tetracarboxylic ester.

UNSATURATED TETRACARBOXYLIC ACIDS.

Dicarbon-Tetracarboxylic Acid,  $\begin{array}{l} C(CO_2H)_2 \\ \| \\ C(CO_2H)_2 \end{array}$. Its tetra-ethyl ester is obtained by letting sodium ethylate act upon chlormalonic ester, and by the action of iodine upon disodium malonic ester (*Berichte*, 17, 2781). Its ester crystallizes in large plates, melting at 58°, and boiling near 325°. The free acid is unstable.

α-**Propylene Tetracarboxylic Acid,** $C_7H_8O_8 =$  $\begin{array}{l} CH.CO_2H \\ \| \\ C\begin{array}{l} \diagup CO_2H \\ \diagdown CH(CO_2H)_2. \end{array} \end{array}$ Its ethyl ester is formed from brommaleïc ester and sodium malonic ester. The acid contains two molecules of water of crystallization. These escape at 100°. The anhydrous acid melts at 191°, with decomposition into CO_2 and pseudo-aconitic acid (p. 473) (*Annalen*, 229, 89).

β-**Propylene-Tetracarboxylic Acid,** $CH(CO_2H)_2.CH:C(CO_2H)_2$, dicarboxyl-glutaconic acid. Its ethyl ester results from the interaction of sodium malonic ester and chloroform. When saponified with hydrochloric acid it yields glutaconic acid. Sodium amalgam converts it into dicarboxyl-glutaric ester. It splits off alcohol and then condenses to a pyrone derivative (*Berichte*, 22, 1419).

PENTAVALENT (PENTAHYDRIC) COMPOUNDS.

Arabite, $C_5H_{12}O_5 = CH_2OH.(CH.OH)_3.CH_2OH$, normal pentaoxypentane, is formed from its aldehyde arabinose, $C_5H_{10}O_5$, by the action of sodium amalgam. It crystallizes from hot alcohol in shining needles, melting at 102°. It has a sweet taste but does not reduce Fehling's solution.

Arabinose, $C_5H_{10}O_5 = CH_2(OH).(CH.OH)_3.CHO$, is its aldehyde. This was formerly thought to be a glucose, $C_6H_{12}O_6$, although it contains but five C-atoms, and belongs to the group of *pentaglucoses* or *pentoses* (p. 497). It is made from gum arabic (also from other gums which yield no, or at least but traces of, mucic acid, when oxidized by nitric acid) on boiling with dilute sulphuric acid (*Berichte*, 19, 3030).

It crystallizes in shining prisms that melt at 100°. It is dextro-rotatory, is slightly soluble in cold water, has a sweet taste (less than that of cane sugar) and reduces Fehling's solution, but is not fermented by yeast. Oxidation converts it into arabonic acid, $C_6H_{10}O_6$ (p. 484) and trioxyglutaric acid. Boiling mineral acids convert it into furfurol, and not into lævulinic acid (as in the case of the carbohydrates).

Two molecules of phenylhydrazine and arabinose (like the glucoses) unite and form a phenylosazone, $C_5H_8O_3(N_2H.C_6H_5)_2$, melting at 158° (*Berichte*, 20, 345). Hydrocyanic acid, etc., converts it into *l*-mannonic and *l*-gluconic acids (p. 490). The constitution of arabinose is thus established (*Berichte*, 20, 341, 1234). Sodium amalgam converts it into arabite.

Xylose, $C_5H_{10}O_5$, is alloisomeric with arabinose. It is obtained by boiling wood-gum (beech-wood, jute, etc.) with dilute acids (*Berichte*, 22, 1046; 23, Ref. 15). It is perfectly similar to arabinose, and has also been included in the group of pentaglucoses. It assumes a cherry-red coloration when digested with phloroglucin and hydrochloric acid. Its *phenylosazone*, like that of arabinose, melts at 160°. Nitric acid oxidizes it to trioxyglutaric and trioxybutyric acids.

Pentaoxyhexane, $C_6H_{14}O_5 = CH_3(CH.OH)_4.CH_2.OH$, is an homologous pentahydric alcohol. It is rhamnite. (*Berichte*, 23, 3103). Its aldehyde is

Rhamnose, $C_6H_{12}O_5 = CH_3(CH.OH)_4CHO$, or Isodulcite. It results upon decomposing different glucosides (quercitrine, xanthoramnine, hesperidine) with dilute sulphuric acid. It forms large vitreous crystals containing one molecule of water. It melts at 93°. The crystals lose water at 100°, and form $C_6H_{12}O_5$. By the absorption of water they revert to $C_6H_{14}O_6$. Isodulcite yields α-methylfurfurol when distilled with sulphuric acid (*Berichte*, 22, Ref. 751).

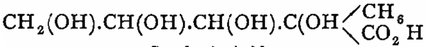
In its properties rhamnose resembles the glucoses, and (with arabinose and xylose) is included under the *Pentoses* (p. 497). It reduces alkaline copper solutions, but is not fermented by yeast. Being an aldehyde-alcohol it combines with two molecules of phenylhydrazine to form an *osazone*, $C_6H_{10}O_3(N_2H.C_6H_5)_2$, melting at 180°. Its *phenylhydrazone*, $C_6H_{12}O_4(N_2H.C_6H_5)$, melts at 159° (*Berichte*, 20, 2575). Hydrocyanic acid and hydrochloric acid convert it into rhamnose carboxylic acid, $CH_3.(CH.OH)_4.CH(OH).CO_2H$ (p. 491). Nitric acid oxidizes it to trioxyglutaric acid (p. 485) (*Berichte*, 22, 1702).

Quercite, $C_6H_{12}O_5$, and **Pinite**, $C_6H_{12}O_5$, are two pentahydric derivatives similar to arabite and the various sugars. The latest researches show that they belong to the benzene series; they will, therefore, be discussed under the polyhydric phenols.

MONOBASIC ACIDS.

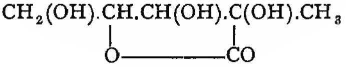
Arabonic Acid, $C_5H_{10}O_6 = CH_2(OH).(CH.OH)_3.CO_2H$, tetraoxyvaleric acid, is obtained by the action of bromine water or nitric acid upon arabinose (*Berichte*, 21, 3007). When liberated from its salts by mineral acids, it splits off water and becomes the lactone $C_5H_8O_5$ (*Berichte*, 20, 345). Further oxidation changes it to trioxyglutaric acid. Its phenylhydrazide melts at 215°.

Saccharic Acid, $C_6H_{12}O_6$, tetraoxycaproic acid, readily changes, when free, into **Saccharin**, its lactone :—



$$CH_2(OH).CH(OH).CH(OH).C(OH\left\langle\begin{matrix}CH_6\\CO_2H\end{matrix}\right.$$

Saccharic Acid.



Saccharin.

Calcium saccharate is obtained by boiling dextrose and lævulose (or from invert sugar) with milk of lime. As soon as the acid is liberated from its salts it decomposes into water and saccharin (*Berichte*, 15, 2954). The latter dissolves with difficulty in water (in 18 parts), forms large crystals, tastes bitter, melts at 160° and sublimes without decomposition. It is reduced to α-methylvalerolactone (365) when heated with hydriodic acid and phosphorus.

Aqueous saccharin possesses right-rotatory power; the salts are lævo-rotatory. Nitric acid oxidizes it to saccharonic acid (p. 485). Oxidized with silver oxide it yields glycollic, oxalic and also acetic acids. Boiling potash produces lactic acid. Lævulinic acid is not formed by the action of hydrochloric acid (*Berichte*, 18, 1334). It yields a phenylhydrazide with phenylhydrazine. It melts at 165°.

Isomerides of saccharin :—

Isosaccharin, $C_6H_{10}O_5$, results from the action of lime upon milk sugar and maltose (*Berichte*, 18, 631). It is very similar to saccharin, and when heated with HI and phosphorus it also yields α-methylvalerolactone. However, it does not yield acetic acid with silver oxide, and when acted upon by nitric acid it forms dioxypropenyl tricarboxylic acid (p. 486). See *Berichte*, 18, 2514, upon the constitution of isosaccharic acid.

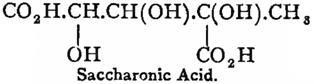
Metasaccharin, $C_6H_{10}O_5$, is found in small quantities together with the preceding (*Berichte*, 18, 642). It crystallizes in plates and melts at 142°. Hydriodic acid and phosphorus reduce it to normal caprolactone (p. 364). Nitric acid oxidizes it to trioxyadipic acid, $C_6H_{10}O_7$.

DIBASIC ACIDS.

Aposorbic Acid, $C_5H_8O_7 = C_3H_3(OH)_3\Big\langle\begin{matrix}CO_2H\\CO_2H,\end{matrix}$ is produced on oxidizing sorbine with nitric acid. It crystallizes in small leaflets which melt with decomposition at 110°. It is easily soluble in water.

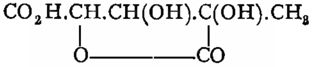
Trioxyglutaric Acid, $C_5H_8O_7 = (CH.OH)_3\Big\langle\begin{matrix}CO_2H\\CO_2H\end{matrix}$, appears to be different from the preceding. It is found when arabinose, sorbinose and rhamnose are oxidized with nitric acid (*Berichte*, 22, 1698). The free acid crystallizes in small plates, that melt at 118–120°.

Saccharon, $C_6H_8O_6$, is the lactone of **Saccharonic Acid,** $C_6H_{10}O_7$:—



$$\begin{array}{l}CO_2H.CH.CH(OH).C(OH).CH_3\\ \quad\;\;|\qquad\qquad\quad\;\;|\\ \quad OH\qquad\qquad CO_2H\end{array}$$

Saccharonic Acid.



$$\begin{array}{l}CO_2H.CH.CH(OH).C(OH).CH_3\\ \quad\;\;|\qquad\qquad\quad\;\;|\\ \quad O\text{————————}CO\end{array}$$

Saccharon.

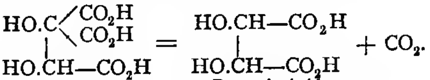
Both are formed when saccharin is oxidized by nitric acid (*Annalen*, 218, 363).

The acid is quite soluble in water. It forms large crystals. In the dessicator or when heated to 90° it breaks up into water and saccharon, which yields salts, $C_6H_7MeO_6$, with carbonates. On boiling, with HI and phosphorus, it is reduced to α-methyl glutaric acid (p. 420).

Trioxyadipic Acid, $C_6H_{10}O_7 = C_4H_5(OH)_3\Big\langle\begin{matrix}CO_2H\\CO_2H\end{matrix}$, results from the oxidation of metasaccharin (see above) with dilute HNO_3 (*Berichte*, 18, 1555). It crystallizes in small laminæ, and melts at 146° with decomposition. It is not capable of forming a lactonic acid. Heated with HI and phosphorus it is reduced to adipic acid, $C_4H_8(CO_2H)_2$.

TRIBASIC ACIDS.

Desoxalic Acid, $C_5H_6O_8 = C_2H(OH)_2(CO_2H)_3$, dioxyethenyl tricarboxylic acid. Its tri-ethyl ester, $C_5H_3(C_2H_5)_3O_8$, results from the action of sodium amalgam upon diethyl oxalate. Large, shining prisms, which melt at 85°. Soluble in 10 parts water and readily in ether. The free acid is obtained by saponifying the ester with baryta water, decomposing the salt with sulphuric acid and slowly evaporating the solution at 40°. The product is a crystalline, deliquescent mass. When its aqueous solution is evaporated or when its ester is heated with water or dilute acids to 100°, the acid yields carbon dioxide and racemic acid: $C_6H_6O_6 = C_4H_8O_6 + CO_2$. Acid radicals can be substituted for the two hydroxyl groups of the desoxalic ester. Heated with hydriodic acid desoxalic acid gives off carbon dioxide, and is reduced to succinic acid. Its structure and transformation into racemic acid are expressed by the following formulas:—



$$\begin{array}{l}HO.C\Big\langle\begin{matrix}CO_2H\\CO_2H\end{matrix}\\ \quad\;\;|\\ HO.CH—CO_2H\end{array} = \begin{array}{l}HO.CH—CO_2H\\ \quad\;\;|\\ HO.CH—CO_2H\end{array} + CO_2.$$

Desoxalic Acid. Racemic Acid.

Oxycitric Acid, $C_6H_8O_8 = C_3H_3(OH)_2.(CO_2H)_3$, dioxytricarballylic acid, accompanies aconitic, tricarballylic and citric acids in beet juice, and is produced by boiling chlorcitric acid (from aconitic acid and ClOH) with alkalies or water (*Berichte*, 16, 1078).

Dioxypropenyl Tricarboxylic Acid, $C_6H_8O_8 = C_3H_3(OH)_2(CO_2H)_3$, results from the oxidation of isosaccharin with nitric acid. It is a thick syrup. At 100° it loses carbon dioxide, and forms dioxyglutaric acid, $C_3H_4(OH)_2.(CO_2H)_2$, which is different from the dioxyglutaric acid obtained from glutaconic acid (*Berichte*, 18, 2514). Hydriodic acid and phosphorus convert it into glutaric acid, $C_3H_6(CO_2H)_2$.

Propenyl Pentacarboxylic Acid, $C_8H_8O_{10} = C_3H_3(CO_2H_5)$, is a pentabasic acid. Its ethyl ester is formed by the action of sodium malonic ester upon chlorethenyl tricarboxylic ester (p. 471).

HEXAVALENT (HEXAHYDRIC) COMPOUNDS.

$C_6H_8(OH)_6$	$C_5H_6\left\}\begin{matrix}(OH)_5\\ CO_2H\end{matrix}\right.$	$C_4H_4\left\}\begin{matrix}(OH)_4\\ (CO_2H)_2.\end{matrix}\right.$
Mannitol, Dulcitol, Sorbite.	Mannonic Acid, Gluconic Acid.	Saccharic Acid, Mucic Acid.

Since in all alcohols each carbon atom bears but one hydroxyl group, we conclude that in the hexahydric alcohols, mannitol and dulcitol, the six hydroxyl groups are attached to 6 different carbon atoms. Mannitol, dulcitol and sorbite are reduced to secondary hexyl iodide when heated with hydriodic acid (p. 95):—

$$C_6H_8(OH)_6 + 11HI = C_6H_{13}I + 6H_2O + 5I_2.$$

The three are, therefore, derivatives of normal hexane, C_6H_{14}, and normal hexoxy-hexane, $C_6H_8(OH)_6 = CH_2(OH)(CH.OH)_4.CH_2.OH$. They are examples of alloisomerism. To explain them, it will be necessary to introduce stereochemical considerations.

According to LeBel and vant' Hoff's theory upon asymmetric carbon atoms, the presence of one asymmetric C-atom determines the existence of two modifications, differing chiefly in their opposite optical rotatory power. In the sexivalent hexaoxyhexane there are four such asymmetrical carbon atoms; hence, a number of modifications are possible. In fact, recent research has shown that we have not only ordinary, right-rotatory or *d*-mannitol, but also a lævo-variety, and further that these may combine to inactive, *i*-mannitol. The latter is *identical* with so-called *a*-acrite, derived from synthetic *a*-acrose. In this manner, it has been possible to effect the *synthesis* of the *compounds* of the *mannitol series* (*Berichte*, 23, 373).

The *hexahydric* alcohols approach the sugars very closely in their properties. They have a very sweet taste. They differ from them in that they do not reduce an alkaline copper solution and are not fermented by yeast. Their optical activity can only be observed after the addition of borates. Moderate oxidation converts them into glucoses, $C_6H_{12}O_6$. They are obtained from the latter by the action of sodium amalgam.

1. **Mannitol or Mannite**, $C_6H_{14}O_6$, exists in three modifications: dextro-, lævo-, and inactive mannitol (see above). The ordinary, or *d*-mannitol, occurs rather frequently in plants and in the manna-ash (*Fraxinus ornus*), whose dried sap is *manna*. It is produced in the mucous fermentation of the different varieties of sugar, and may be artificially prepared by the action of sodium amalgam upon *d*-mannose and fruit-sugar, and with more difficulty from grape sugar (*Berichte*, 17, 227): $C_6H_{12}O_6 + H_2 = C_6H_{14}O_6$. Mannitol is also obtained by extracting manna with alcohol and allowing the solution to crystallize.

Mannitol forms delicate needles or rhombic prisms; it dissolves in 6.5 parts of water at 16°, and readily in boiling alcohol. It possesses a very sweet taste and melts at 166°. Its solution is dextrorotatory in the presence of borax. When oxidized with care, it yields fruit-sugar (called mannitose, *Berichte*, 20, 831), and mannose (*Berichte*, 21, 1805). Nitric acid oxidizes mannitol to saccharic acid and oxalic acid. Hydriodic acid converts it into hexyl iodide (p. 486).

When mannitol is heated to 200° it loses water and forms the anhydrides, *Mannitan*, $C_6H_{12}O_5$, and *Mannide*, $C_6H_{10}O_4$. The latter is also obtained by distilling mannitol in a vacuum. It melts at 87° and boils at 274° (*Berichte*, 17, Ref. 108).

Mannitol resembles the sugars in combining with bases to yield compounds like $C_6H_{14}O_6.CaO$. When heated with organic acids mannitan esters are usually produced:—

$$\underset{\text{Mannitol.}}{C_6H_{14}O_6} + \underset{\text{Stearic Acid.}}{4C_{18}H_{36}O_2} = \underset{\text{Mannitan Stearate.}}{C_6H_8(C_{18}H_{35}O)_4O_5} + 5H_2O.$$

The hexacetate of mannitol, $C_6H_8(O.C_2H_3O)_6$, is produced by heating mannitol with acetic anhydride; it is crystalline and melts near 100°.

Mannitol dichlorhydrin, $C_6H_8\left\{\begin{matrix}(OH)_4\\ Cl_2\end{matrix}\right.$, is formed when mannitol is heated with concentrated hydrochloric acid. It consists of laminæ, melting at 174°. Hydrobromic acid yields the dibromhydrin, $C_6H_8\left\{\begin{matrix}(OH)_4\\ Br_2\end{matrix}\right.$, melting at 178°.

Nitro-mannite, $C_6H_8(O.NO_2)_6$, is obtained by dissolving mannitol in a mixture of concentrated nitric and sulphuric acids. It crystallizes from alcohol and ether in bright needles; it melts when carefully heated and deflagrates strongly. When struck it explodes very violently. Alkalies and ammonium sulphide regenerate mannitol.

Lævo-mannitol, $C_6H_{14}O_6$, *l*-Mannite, is obtained by the reduction of *l*-mannose (from arabinose carboxylic acid, p. 488) in weak alkaline solution with sodium amalgam (*Berichte*, 20, 375). It is quite similar to ordinary mannite, but melts a little lower (163–164°), and in the presence of borax is lævorotatory.

Inactive Mannitol, $C_6H_{14}O_6$, *i*-Mannite, is produced in a similar manner, from inactive mannose (from *i*-mannonic acid). It is identical with the synthetically prepared *a*-acrite (from *a-acrose*, p. 499) (*Berichte*, 23, 383). It resembles ordinary mannitol, melts 3° higher (at 168°), and in aqueous solution is inactive even in the presence of borax. Nitric acid oxidizes it to inactive mannose and inactive mannonic acid. The latter can be resolved into *d*- and *l*-mannonic acids (*Berichte*, 23, 391).

2. **Dulcitol, Dulcite,** $C_6H_{14}O_6$, occurs in various plants and is obtained from dulcitol-manna (originating from Madagascar manna). It is made artificially by the action of sodium amalgam upon milk sugar and galactose. It crystallizes in large monoclinic prisms, having a sweet taste. It dissolves in water with more difficulty than mannite, and is almost insoluble in boiling alcohol. It melts at 188°. The hexacetate, $C_6H_8(O.C_2H_3O)_6$, melts at 171°. Hydriodic acid converts it into the same hexyl iodide that mannitol yields. Nitric acid oxidizes dulcitol to mucic acid. There is also an intermediate aldehyde compound that combines with two molecules of phenylhydrazine and forms the *osazone*, $C_6H_{10}O_4(N_2H.C_6H_5)_2$ (*Berichte*, 20, 1091).

(3) **Sorbite,** $C_6H_{14}O_6 + H_2O$, occurs in mountain-ash berries, forming small crystals which dissolve readily in water. When heated they lose water and melt near 110°. It is reduced to secondary hexyl iodide (*Berichte*, 22, 1048) when heated with hydriodic acid and phosphorus. It corresponds, in all probability, to grape sugar (*Berichte*, 23, 2623).

HEXAVALENT (HEXAHYDRIC) ALDEHYDES AND KETONES.

When the hexahydric alcohols, $C_6H_{14}O_6$, are carefully oxidized, they lose two atoms of hydrogen, and are converted into their aldehydes and ketones. These products are identical with the glucoses that occur naturally as such and are treated with these under the carbohydrates. Polyhydric mono- and poly-carboxylic acids result if the alcohols or glucoses are further oxidized :—

$C_6H_{14}O_6$, or	$C_6H_{12}O_6$, or	$C_6H_{12}O_7$, or
$C_5H_6(OH)_5.CH_2.OH$.	$C_5H_6(OH)_5.CHO$.	$C_5H_6(OH)_5.CO_2H$.
Hexahydric Alcohols.	Glucoses.	Monocarboxylic Acid.
Mannitol.	Fruit Sugar, Mannose.	Mannonic Acid, Gluconic Acid.

MONOBASIC ACIDS.

The penta-oxy-monocarboxylic acids are produced by the further oxidation of the alcohols and glucoses corresponding to them. They may also be obtained synthetically from the pentoses (arabinose, rhamnose, p. 483) by the aid of HCN, etc. (p. 494) :—

$C_5H_{10}O_5$	yields	$C_5H_6(OH)_5.CO_2H$.
Arabinose.		Arabinose Carboxylic Acid.

Being γ-oxy-derivatives, nearly all of these acids are very unstable when in a free condition. They lose water readily and pass into *lactones* (p. 352): $C_6H_{12}O_7 = C_6H_{10}O_6 + H_2O$. When acted upon in acid solution by sodium amalgam, these lactones (not the acids) reabsorb two atoms of hydrogen, and are converted into the corresponding glucoses (E. Fischer, *Berichte*, **22**, 2204; **23**, 370, 799, 930) (p. 494): $C_6H_{10}O_6 + H_2 = C_6H_{12}O_6$.

Thus, the three mannonic acids yield three mannoses, the three gluconic acids three glucoses, and galactonic acid galactose.

These acids (like other carboxylic acids), when acted upon with one molecule of phenylhydrazine, lose the hydroxyl of the carboxyl group, and form characteristic *phenylhydrazides*, $C_6H_{11}O_6.N_2H_2.C_6H_6$ (p. 495). The latter generally result on heating the acids (1 part) with phenylhydrazine (1 part), water (10 parts), and 50 per cent. acetic acid (1 part). They usually separate from the solution in a crystalline form (*Berichte*, **22**, 2728). They are resolved into their components when boiled with alkalies. They are distinguished from the hydrazones of the aldehydes and ketones by the reddish-violet coloration produced upon mixing them with concentrated sulphuric acid and a drop of ferric chloride.

These acids are reduced to normal caprolactone, if they are heated with hydriodic acid and phosphorus (p. 364). They must, therefore, be considered as pentaoxycaproic acids, having the same structural formula, $C_5H_6(OH_5).CO_2H$, and are physical or geometrical isomerides (p. 486). Gluconic and mannonic acids also occur in dextro- and lævo-rotatory modifications. These unite and produce inactive forms (*Berichte*, **23**, 371, 2623).

1. **Mannitic Acid**, $C_6H_{12}O_7$, is obtained by the action of platinum black upon aqueous mannitol. It is a very soluble gummy mass which reduces Fehling's solution (*Berichte*, **23**, 3223).

2. **Gluconic Acid**, $C_6H_{12}O_7$, exists in a dextro-, a lævo- and an inactive form. *d*-**Gluconic Acid** is formed by the oxidation of dextrose, cane sugar, dextrine, starch and maltose with chlorine or bromine water, and is most readily obtained from glucose (*Berichte*, **17**, 1298). Gluconic acid, separated from its lead salt by hydrogen sulphide, forms a syrup which is almost insoluble in alcohol. When evaporated, or upon standing, it changes in part to its crystalline lactone, $C_6H_{10}O_6$, melting at 130–135°. Its barium salt crystallizes with three molecules of water, the calcium salt with one. The acid is dextro-rotatory, but does not reduce Fehling's solution.

Its *phenylhydrazide*, $C_6H_{11}O_6(N_2H_2.C_6H_5)$, crystallizes in brilliant leaflets and prisms. When rapidly heated it melts about 200° (*Berichte*, **23**, 802, 2625).

When *d*-gluconic acid is heated to 140° with quinoline it is converted into *d*-mannonic acid. And, the latter, when similarly treated, becomes *d*-gluconic acid. A state of equilibrium occurs in this case similar to that observed in the transposition of racemic acid and mesotartaric acid when heated with water (p. 479). If sodium amalgam be allowed to act upon the lactone of gluconic acid, when in a cold, acid solution, it is changed to *grape sugar* (*Berichte*, 23, 804).

l-**Gluconic Acid** is obtained by heating *l*-mannonic acid. This is similar to the formation of *d*-gluconic acid from *d*-mannonic acid (see above). A more convenient course consists in exposing arabinose to the action of CNH, etc. This acid is more soluble than *l*-mannonic acid, and is, therefore, found in the mother liquor from the latter. It is separated by means of its phenylhydrazide, $C_6H_{11}O_6.N_2H_2.C_6H_5$. This melts at 200° (*Berichte*, 23, 2613). Heated to 140° together with quinoline, it is partially converted into *l*-mannonic acid.

i-**Gluconic Acid** (and its lactone) is formed upon evaporating the aqueous solution of a mixture of *d*- and *l*-gluconic acids. Its calcium salt dissolves with difficulty. The acid is inactive. Its *phenylhydrazide* is also inactive. It melts at 190° (*Berichte*, 23, 2618).

The three gluconic acids yield the three corresponding saccharic acids, when they are oxidized with nitric acid (p. 492). The three glucoses result upon their reduction (p. 503).

3. Mannonic Acid, $C_6H_{12}O_7$, occurs as dextro-, lævo- and inactive mannonic acid.

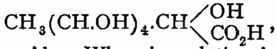
Ordinary or *d*-mannonic acid is produced when ordinary *d*-mannose is oxidized with bromine water. It is obtained pure by boiling its phenylhydrazide with baryta water (*Berichte*, 22, 3220). When the solution is evaporated it solidifies to a crystalline mass. This is the *lactone*, $C_6H_{10}O_6$, which crystallizes from alcohol in long shining needles, melting at 149–153°. The aqueous solution of the lactone is neutral and dextro-rotatory $[\alpha]_D = + 53.8°$. Its *phenylhydrazide*, $C_6H_{11}O_6(N_2H_2.C_6H_5)$ crystallizes from hot water in brilliant prisms, melting at 214–216°. When the acid is heated to 140° together with quinoline, it changes to gluconic acid (see above).

Lævo-mannonic Acid, $C_6H_{12}O_7$, is identical with arabinose-carboxylic acid, obtained from arabinose by the action of hydrocyanic acid, etc. (*Berichte*, 19, 3033). It is further produced, together with *d*-mannonic acid, by the decomposition of *i*-mannonic acid. When its solution is concentrated it passes into the *lactone*, $C_6H_{10}O_6$. The latter crystallizes from alcohol in needles that dissolve with difficulty. They become soft at 140–150°. Its solution is lævo-rotatory $[\alpha]_D = 54.8°$. The phenylhydrazide of *l*-mannonic acid is very similar to that of *d*-mannonic acid. It also melts at 214–216°. *l*-Mannose and *l*-mannitol result from the reduction of *l*-mannonic lactone (p. 487).

Inactive Mannonic Acid, $C_6H_{12}O_7$, *i*-mannonic acid, is obtained by the union of equal parts of *d*- and *l*-mannose. Its *lactone*, $C_6H_{10}O_6$, separates in colorless radiating crystals, when the solution is evaporated. When the latter is concentrated the crystals assume a prism form. The lactone melts somewhat higher than its components, softens at 149° and fuses at 155°. The *phenylhydrazide* of the acid crystallizes from hot water in forms similar to those of sodium chloride. When rapidly heated it melts at 230°. The acid can be resolved into its components if it be fermented by penicillium glaucum, or by the crystallization of the strychnine salt. Sodium amalgam converts it into *i*-mannose and *i*-mannite, which is identical with *α*-acrite—prepared synthetically from *α*-acrose. If *i*-mannite be oxidized with nitric acid it yields *i*-mannose, which bromine water can further change to *i*-mannonic acid. Thus, the *synthesis of all the members of the mannite series has been realized* (*Berichte*, 23, 391).

When the mannonic acids are oxidized with nitric acid they yield the corresponding mannosaccharic acids (p. 494).

4. **Lactonic Acid,** $C_6H_{12}O_7$, galactonic acid, is produced from milk sugar, galactose and gum arabic by the action of bromine water (*Berichte*, 18, 1552). It crystallizes, on standing over sulphuric acid, in small needles. Prolonged heating to 100° converts it into the corresponding lactone, $C_6H_{10}O_6$. Its phenylhydrazide crystallizes in brilliant laminæ, melting at 200–205°. Sodium amalgam causes the lactone to revert to galactose (*Berichte*, 23, 935.) It yields mucic acid on oxidation with nitric acid.

Rhamnose-carboxylic Acid, $C_7H_{14}O_7$ = 

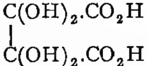
$$CH_3(CH.OH)_4.CH\left\langle\begin{matrix}OH\\CO_2H\end{matrix}\right.$$

, from rhamnose, is homologous with the preceding acids. When its solution is evaporated it leaves the *lactone*, $C_7H_{12}O_6$, a crystalline mass, melting at 162–168° (*Berichte*, 21, 2173). Its phenylhydrazide, $C_7H_{13}O_6.N_2H_2.C_6H_5$, forms six-sided leaflets, melting about 210° (*Berichte* 22, 2733).

When the acid is heated with hydriodic acid and phosphorus it is reduced to normal heptylic acid. Sodium amalgam converts the lactone into methylhexose, $C_7H_{14}O_6 = C_6H_{11}(CH_3)O_6$ (*Berichte* 23, 936).

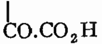
Glycuronic Acid, $C_6H_{10}O_7 = CHO.(CH.OH)_4.CO_2H$, a *tetraoxyaldehydic acid*, is obtained by decomposing euxanthic acid (see this) on boiling with dilute sulphuric acid. Various glucoside-like compounds of glycuronic acid with camphor, borneol, chloral, phenol and different other bodies (*Berichte*, 19, 2919; Ref. 762) occur in urine after the introduction of these compounds into the system. Boiling acids decompose them into their components. Glycuronic acid is a syrup, which rapidly passes into the lactone $C_6H_8O_6$ on warming. The latter consists of large plates, of sweet taste, melting at 169° C. Bromine water oxidizes it to saccharic acid. It also appears that when saccharic acid is reduced glycuronic acid results (*Berichte*, 23, 937).

DIBASIC ACIDS.

1. **Tetra-oxysuccinic Acid,** $C_4H_6O_8$ = 

$$\begin{matrix}C(OH)_2.CO_2H\\|\\C(OH)_2.CO_2H\end{matrix}$$

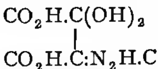
, **Dioxytartaric Acid.**

This was formerly regarded as carboxytartronic acid, $C(OH).(CO_2H)_3$. It is obtained when protocatechuic acid, pyrocatechin and guaiacol, in ethereal solution, are acted upon with N_2O_3, or from nitro-tartaric acid through the action of an alcoholic solution of nitrous acid (*Annalen*, 221, 246). The addition of sodium carbonate to the aqueous solution separates the *sodium salt*, $C_4H_4Na_2O_8 + 2H_2O$, as a sparingly soluble crystalline powder. When heated with water it decomposes into CO_2 and sodium tartronate, $C_3H_2Na_2O_5$. The free acid, obtained from the sodium salt by means of hydrochloric acid and ether, is crystalline. It melts with decomposition at 98° (*Berichte*, 22, 2015). On reducing the acid with zinc and hydrochloric acid, it passes into inactive tartaric acid and racemic acid. This deportment is explained by the fact that tetraoxysuccinic acid represents a diketonic acid, 

$$\begin{matrix}CO.CO_2H\\|\\CO.CO_2H\end{matrix}$$

, which, like glyoxylic acid and mesoxalic acid, contains two molecules of water that may be readily split off.

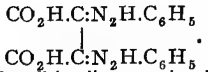
Being a diketonic acid dioxytartaric acid combines with 1 and 2 molecules of phenylhydrazine, forming,



$$\begin{matrix}CO_2H.C(OH)_2\\|\\CO_2H.C:N_2H.C_6H_5\end{matrix}$$

Phenylizine dioxytartaric acid.

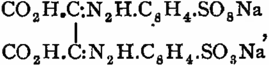
and



$$\begin{matrix}CO_2H.C:N_2H.C_6H_5\\|\\CO_2H.C:N_2H.C_6H_5\end{matrix}.$$

Diphenylizine dioxytartaric acid.

The first melts with decomposition at 218°. The second is an orange yellow powder, yielding yellow salts with bases. Concentrated (fuming) sulphuric acid converts it into a disulpho-acid, which is also formed by the union of dioxytartaric acid with phenylhydrazine-sulphonic acid. The disodium salt of this acid,



$$\begin{array}{l}CO_2H.C{:}N_2H.C_8H_4.SO_8Na \\ \quad\;\;| \\ CO_2H.C{:}N_2H.C_8H_4.SO_3Na\end{array}$$

, is an orange yellow powder. As *Tartrazine*, it is applied as a yellow dye for wool (*Berichte*, 20, 834).

2. Acids, $C_6H_{10}O_8 = C_4H_4(OH)_4(CO_2H)_2$.

There are four known isomeric acids of this formula: saccharic, mucic, isosaccharic and manno-saccharic acids. All are obtained by the oxidation of various carbohydrates with nitric acid, and are readily prepared from the corresponding monocarboxylic acids, $C_5H_6(OH)_5.CO_2H$ (p. 488), upon oxidation with chlorine or bromine water. Gluconic acid yields saccharic acid, galactonic mucic acid, arabinose carboxylic acid, manno-saccharic acid, while the monocarboxylic acid, corresponding to isosaccharic acid, is not known. When reduced by HI and phosphorus all four acids are converted into normal adipic acid, $C_4H_8(CO_2H)_2$; hence all of them must be considered as normal tetraoxyadipic acids. They are physical or stereochemical isomerides.

1. **Saccharic Acid**, $C_6H_{10}O_8$, Acidum saccharicum, like gluconic and mannonic acids, exists in three modifications: dextro-, lævo- and inactive saccharic acid. Ordinary, or *d*-saccharic acid, results in the oxidation of cane sugar, *d*-glucose (grape sugar), *d*-gluconic acid, and many other carbohydrates with nitric acid.

Cane sugar (1 part) is heated with common nitric acid (3 parts) until a stormy reaction sets in, then cooled and heated anew to 50°, until brown vapors cease coming off. The liquid is then diluted with ½ volume of water, saturated with potassium carbonate, and an excess of acetic acid added. In the course of a few days the primary potassium salt will separate in hard crystals, which may be purified by recrystallization from hot water. The free acid is obtained by decomposing the cadmium salt with hydrogen sulphide, or the silver salt with hydrochloric acid (*Berichte*, 21, Ref. 472).

Ordinary, *d*-saccharic acid forms a deliquescent, gummy mass, readily soluble in alcohol. If the pure, syrupy acid be allowed to stand for some time, it changes to its crystalline lactonic acid, $C_6H_8O_7$, that melts at 130–132° (*Berichte*, 21, Ref. 472). When prepared from cane sugar, its solution is lævo-rotatory and reduces ammoniacal silver solutions. It turns brown at 100° and decomposes. When oxidized with nitric acid, dextro-tartaric acid and oxalic acid are formed. Hydriodic acid reduces it to adipic acid.

It forms acid and neutral salts. The *primary potassium salt*, $C_8H_9KO_8$, and the *ammonium salt*, $C_6H_9(NH_4)O_8$, crystallize well and dissolve with difficulty in cold water. The neutral alkali salts are deliquescent; the salts of the heavy metals are insoluble. The *diethyl ester*, $C_4H_4(OH)_4(CO_2.C_2H_5)_2$, is crystalline and is readily soluble in water. With ammonia it forms the *amide*, $C_4H_4(OH)_4(CO.NH_2)_2$, a white powder. When acetyl chloride acts on the ester we obtain the *tetra-acetate*, $C_4H_4(O.C_2H_3O)_4.(CO_2.C_2H_5)_2$, which forms prisms, melting at 61°; insoluble in water. Acetyl chloride, acting upon free saccharic acid, converts it into the *lactone of diacetyl-saccharic acid*, $C_6H_4(O.C_2H_3O)_2O_4$, melting at 188°.

Two molecules of phenylhydrazine and *d*-saccharic acid form a *diphenylhydrazide*, $C_6H_8O_6(N_2H_2.C_6H_5)_2$, that melts at 210° with decomposition (p. 489 and *Berichte*, 21, Ref. 186).

l-Saccharic acid is obtained upon oxidizing *l*-gluconic acid with nitric acid. It is quite similar to *d*-saccharic acid, but is lævorotatory. It also forms a dihydrazide, melting at 214°.

i-Saccharic acid is formed when *i*-gluconic acid is oxidized, or by mixing *d*-saccharic with *l*-saccharic acid. It is inactive and forms a *dihydrazide*, melting at 210°.

The *monopotassium salts*, $C_6H_9O_8K$ (*Berichte*, 23, 2621), are characteristic derivatives of the three saccharic acids.

2. **Mucic Acid**, $C_6H_{10}O_8$, Acidum mucicum, is obtained in the oxidation of dulcitol, milk-sugar, galactose, galactonic acid and nearly all the gum varieties.

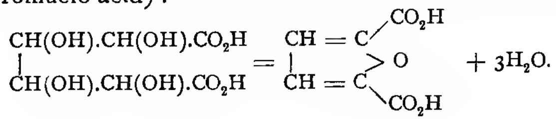
Preparation.—Heat 100 grams of lactic acid with 1200 c.c. of nitric acid (sp. gr. 1.15), until the volume is reduced to 200 c.c. Cool, and wash the mucic acid that is formed with water (*Berichte*, 227, 224).

It is a white crystalline powder, soluble in 60 parts of boiling water. It is almost insoluble in cold water and alcohol. It melts at 210° with decomposition. When boiled for some time with water it passes into an isomeric paramucic acid. Boiling nitric acid decomposes it into racemic acid and oxalic acid. Hydriodic acid reduces it to adipic acid.

The *neutral potassium salt* and *ammonium salt*, $C_6H_8(NH_4)_2O_8$, crystallize well and dissolve with difficulty in cold water; the *primary* salts dissolve readily. The *silver salt*, $C_6H_8Ag_2O_8$, is an insoluble precipitate. When heated the neutral ammonium salt decomposes into NH_3, water and pyrrol, C_4H_5N.

The *diethyl ester*, $C_4H_4(OH)_4(CO_2.C_2H_5)_2$, is obtained by heating mucic acid and alcohol with sulphuric acid. It is crystalline, is soluble in hot water and melts at 158°. Acetyl chloride converts it into the tetra-acetate, which melts at 177°. The free acid also forms a tetra-acetyl compound (*Berichte*, 21, Ref. 186).

The ready conversion of mucic acid into furfurane derivatives is rather remarkable. Digestion with fuming hydrochloric or hydrobromic acid changes it to furfurane dicarboxylic acid (dehydromucic acid):—



When mucic acid is heated alone it splits off carbon dioxide and becomes furfane monocarboxylic acid (pyromucic acid):—

$$C_4H_4(OH)_4(CO_2H)_2 = C_4H_3O.CO_2H + 3H_2O + CO_2.$$

Heated with barium sulphide it passes in like manner into *a*-thiophene carboxylic acid (*Berichte*, 18, 456).

3. **Isosaccharic Acid,** $C_6H_{10}O_8$ (see above), results from HCl-glucosamine (p. 505) upon oxidizing it with nitric acid (*Berichte*, 19, 1258). It is very soluble in water and alcohol, forms rhombic crystals and melts at 185°. Its solution is dextrorotatory; $(a)_D = 46.1°$. Its *diethyl ester*, $C_6H_8O_8(C_2H_5)_2$, melts at 73°. Acetyl chloride converts the ester into the tetra-acetyl compound, $C_6H_4(O.C_2H_3O)_4.(CO_2.C_2H_5)_2$, melting at 47°. Hydriodic acid reduces isosaccharic acid to normal adipic acid (see above).

Like mucic acid it yields furfane derivatives. It breaks up into water, carbon dioxide and pyromucic acid when distilled. Dehydromucic acid is formed on heating isosaccharic acid in a current of hydrogen chloride. Pyromucic acid and *a*-thiophene carboxylic acid are produced when the iso-acid is heated with barium sulphide. When its *diethyl ester* is heated with alcoholic ammonia *anhydro-diamide*, $C_4H_4O.(OH)_2.(CO.NH_2)_2$, is produced; this by distillation yields pyromucamide, $C_4H_3O.CO.NH_2$ (*Berichte*, 19, 1277).

4. **Metasaccharic Acid,** $C_6H_{10}O_8$, *l*-mannosaccharic acid, is produced by oxidizing arabinose carboxylic acid with nitric acid (*Berichte*, 20, 2710; 23, 2131). On evaporating the solution, its *double lactone*, $C_6H_6O_6 + 2H_2O$, crystallizes. It has a neutral reaction, and on standing over sulphuric acid loses two molecules of water. When air-dried it melts at 68°, and when anhydrous, at 180°. Hydriodic acid reduces it to adipic acid. Sodium amalgam converts it into mannite, $C_6H_{14}O_6$ (*Berichte*, 22, 2204).

The *diphenylhydrazide* of metasaccharic acid, $C_4H_4(OH)_4.(CO.N_2H_2.C_6H_5)_2$, is produced on heating the double lactone with phenylhydrazide and sodium acetate. It melts at 213°. Concentrated sulphuric acid and ferric chloride color it red (p. 489). Acetic anhydride converts the double lactone into the diacetyl derivative, $C_6H_4O_6(C_2H_3O)_2$, melting at 155° (*Berichte*, 21, 1422; 22, 524).

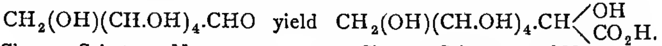
Butane Hexacarboxylic Acid, $C_{10}H_{10}O_{12} = C_4H_4(CO_2H)_6$, is a hexabasic acid. Its hexa-ethyl ester is formed by the action of iodine upon the sodium compound of ethenyl tricarboxylic ester (p. 471). It forms hexagonal plates, which melt at 56° (*Berichte*, 17, 2786).

HEPTAVALENT (HEPTAHYDRIC) COMPOUNDS.

Perseïte, $C_7H_{16}O_7 = C_7H_9(OH)_7$, is an heptahydric alcohol. It is found in the leaves and seeds of *Laurus persea*. It is artificially prepared by reducing its aldehyde mannoheptose, $C_7H_{14}O_7$ (p. 507), with sodium amalgam (*Berichte*, 23, 935). It crystallizes in needles, melting at 184°. At 250° it parts with water, and forms a compound resembling mannitan. It does not reduce Fehling's solution, and is not fermented by yeast. Nitric acid reoxidizes it to mannoheptose.

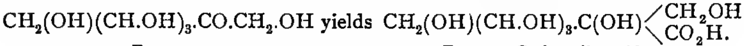
The *heptahydric aldehydes*, $C_7H_{14}O_7$, resemble the sugars in their behavior. They will be discussed with them under the designation of *heptoses* (p. 507).

The *heptahydric monocarboxylic acids*, $C_7H_{14}O_8$, are obtained synthetically from the hexaglucoses or hexoses, $C_8H_{12}O_6$, by the action of hydrocyanic acid, and the subsequent transformation of the oxycyanides first formed (Kiliani, *Berichte*, **19**, 767; **21**, 915. E. Fischer, *Berichte*, **22**, 370):—



$$CH_2(OH)(CH.OH)_4.CHO \text{ yield } CH_2(OH)(CH.OH)_4.CH{<}\begin{matrix}OH\\CO_2H.\end{matrix}$$

Glucoses, Galactoses, Mannoses. Glucose-, Galactose-, and Mannose-Carboxylic Acid.



$$CH_2(OH)(CH.OH)_3.CO.CH_2.OH \text{ yields } CH_2(OH)(CH.OH)_3.C(OH){<}\begin{matrix}CH_2OH\\CO_2H.\end{matrix}$$

Fructose. Fructose-Carboxylic Acid.

Glucose-, galactose-, and mannose-carboxylic acids have the same constitutional formulas. They also yield normal heptylic acid, $C_6H_{13}.CO_2H$, when reduced with hydriodic acid and phosphorus. Therefore, they are either to be considered as physical or stereochemical isomerides.

Like other carboxylic acids, all of these acids combine with phenylhydrazine to form phenylhydrazides, $C_7H_{13}O_7.N_2H_2.C_6H_5$, which are distinguished from the phenylhydrazones by the violet coloration they give when acted upon with sulphuric acid and ferric chloride (*Berichte*, **22**, 2728).

Sodium amalgam reduces these acids (their lactones) to the corresponding aldehydes or aldoses, $C_7H_{14}O_7$ (this is similar to the reduction of the pentaoxy-monocarboxylic acids to the hexoses, $C_6H_{12}O_8$, p. 489):—

$$CH_2(OH).(CH.OH)_5.CO_2H \quad \text{yields} \quad CH_2(OH)(CH.OH)_5.CHO.$$

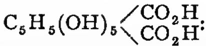
These are the higher synthetic varieties of sugar—the *heptoses*. From the latter, it is possible, by similar reactions, to obtain the heptocarboxylic acids and the *octoses*, corresponding to them (E. Fischer, *Berichte*, **22**, 2204; **23**, 930).

Glucose-carboxylic Acid, $C_7H_{14}O_8$, hexaoxyheptylic acid, is obtained from dextrose (grape sugar) by means of CNH, etc. The lactone, $C_7H_{12}O_7$, crystallizes from the concentrated solution. This is a neutral substance, that dissolves readily in water. It softens about 145°. Hydriodic acid and phosphorus reduce it to heptolactone, $C_7H_{12}O_2$, and normal heptylic acid. Sodium amalgam reduces the lactone to *dextroheptose* (glucoheptose) (p. 507) (*Berichte*, **23**, 936). The phenylhydrazide of dextrose-carboxylic acid melts at 171°. Pentaoxypimelic acid (p. 496) is formed when dextrose-carboxylic acid is oxidized with nitric acid.

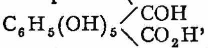
***d*-Mannose-carboxylic Acid**, $C_7H_{14}O_8$, from ordinary *d*-mannose (p. 503), separates from concentrated solutions as a *lactone*, $C_7H_{12}O_7$, in warty crystals. It is very soluble in water, has a neutral reaction, and melts at 148–150°. Hydriodic acid and phosphorus reduce the acid to heptolactone and heptylic acid (see above and *Berichte*, **22**, 370). Its *phenylhydrazide* (see above) melts about 220° with decomposition. Sodium amalgam reduces the lactone to mannoheptose, $C_7H_{14}O_7$, and then to the heptahydric alcohol perseïte, $C_7H_{16}O_7$ (*Berichte*, **23**, 936, 2226).

Galactose-carboxylic Acid, $C_7H_{14}O_8$, from galactose, crystallizes in minute hydrous needles. It has an acid reaction. After the acid has been dried over sulphuric acid it melts at 145°, and passes into its *lactone;* this is also produced on heating the solution. It consists of needles, melting at 150°. Sodium amalgam changes it into galaheptose, $C_7H_{14}O_7$.

Fructose-carboxylic Acid, $C_7H_{14}O_8$, is obtained from lævulose by the action of hydrocyanic and hydrochloric acids (*Berichte*, 19, 222). When oxalic acid acts upon its calcium salt, it liberates a mixture of the acid and its lactone, $C_7H_{12}O_7$. Reduction with hydriodic acid forms heptolactone and heptylic acid, $C_7H_{14}O_2$. The latter is identical with methyl-normal butyl acetic acid (p. 230). Hence it is evident that *lævulose* is a *ketone-alcohol*

Pentaoxy-dicarboxylic Acids,  $C_5H_5(OH)_5\left\langle\begin{matrix}CO_2H\\CO_2H\end{matrix}\right.$.

Pentaoxy-pimelic Acid, $C_7H_{12}O_9$, is produced in the oxidation of dextrose-carboxylic acid with nitric acid. The *lactone* is crystalline, and melts at 143° (*Berichte*, 19, 1917).

Carboxy-galactonic Acid, $C_7H_{12}O_9$, is formed in the oxidation of galactose-carboxylic acid with nitric acid. It dissolves with difficulty in water, crystallizes in plates, and melts at 171° with decomposition (*Berichte*, 22, 523). **Aldehyde-galactonic Acid,** $C_7H_{12}O_8$ =  $C_6H_5(OH)_5\left\langle\begin{matrix}COH\\CO_2H\end{matrix}\right.$, is a transition product in the formation of the preceding acid. It is an analogue of glycuronic acid (p. 491) (*Berichte*, 22, 1385).

Butane-heptacarboxylic Acid, $C_4H_3(CO_2H)_7$, is a heptacarboxylic acid, formed by the action of chlormalonic ester, $CHCl(CO_2R)_2$, upon sodium propenyl-pentacarboxylic ester (p. 486). It boils at 280–285° under a pressure of 130 mm.

Higher polycarboxylic esters have been prepared in an analogous manner (*Berichte*, 21, 2113):—

Hexane decacarboxylic Ester, $C_6H_4(CO_2R)_{10}$, is produced by the action of chlor-propenyl-pentacarboxylic ester (p. 486) upon sodium-propenyl-pentacarboxylic ester. It is a yellow oil.

Octan-tesserakaideca-carboxylic Acid, $C_8H_4(CO_2R)_{14}$, is the highest polycarboxylic acid that has been prepared. It is obtained from sodium butane-heptacarboxylic ester and chlorbutane-heptacarboxylic ester. It is a thick oil (*Berichte*, 21, 2113).

OCTO- AND NONO-HYDRIC COMPOUNDS.

d-**Manno octite,** $C_8H_{18}O_8$, is an octohydric alcohol. It is produced when *d*-mannoctose is reduced with sodium amalgam. It dissolves with difficulty in water, crystallizes in small plates, melts at 258°, and sublimes without decomposition. Its aldehyde is described on p. 507 as *manno-octose.*

d-**Manno-octonic Acid,** $C_8H_{16}O_9$, has been obtained as a syrup by the action of CNH, etc, upon *d*-mannoheptose, $C_7H_{16}O_7$. Its hydrazide, $C_8H_{15}O_8.N_2H_2.C_6H_5$, is crystalline, and melts at 243°. The *lactone*, $C_8H_{14}O_8$, has a neutral reaction, a sweet taste, and melts about 168°. By reduction it forms *d*-mannoctose (*Berichte*, 23, 2234).

d-**Mannononite,** $C_9H_{20}O_9$, is a nono-hydric alcohol. It may be prepared by reducing its aldehyde, *mannononose*, $C_9H_{18}O_9$ (p. 507) with sodium amalgam.

d-**Manno-nononic Acid,** $C_9H_{18}O_{10}$, has been obtained from manno-octose,

$C_8H_{16}O_8$, by means of CNH, etc. Its hydrazide, $C_9H_{17}O_9.N_2H_2.C_6H_5$, dissolves with difficulty, and melts about 254°. Its *lactone*, $C_9H_{16}O_9$, forms minute needles, melting at 176°. When reduced it forms *d*-manno-nonose, $C_9H_{18}O_9$ (p. 507) (*Berichte*, 23, 2236).

CARBOHYDRATES.

This term is applied to a large class of compounds, widely distributed in nature. They contain six, or a multiple of six carbon atoms. The ratio of their hydrogen and oxygen atoms is the same as that of these elements in water. The carbohydrates may be arranged into three groups: the glucoses, $C_6H_{12}O_6$, grape sugar and fruit sugar; the sugars, $C_{12}H_{22}O_{11}$, or disaccharides, as cane sugar; and the polysaccharides $(C_6H_{10}O_5)_n$, as starch and dextrine. The glucoses were discovered to be the aldehyde- or ketone-derivatives of the hexahydric alcohols (chiefly through the investigations of Kiliani (1885) upon the hydrogen cyanide addition-products), into which they might be converted by the absorption of two hydrogen atoms. Consequently, they could be produced by the oxidation of the alcohols. The di- and polysaccharides proved to be ethereal anhydrides of the glucoses (similar to polyglycols, p. 304); inasmuch as all of them could be converted into the glucoses by hydrolytic decomposition. The more recent and widely extended researches of E. Fischer have amplified these views quite considerably, and in many cases modified them very materially (*Berichte*, 23, 2114). The glucose character of a compound is very much affected by its constitution, as aldehyde alcohol—CH(OH).CHO, or ketone alcohol—$CO.CH_2.OH$, and we thus have glucoses containing not only *six*, but even a less or greater number of carbon and oxygen atoms. According to the number of the oxygen atoms, they are known as *pentoses*, *hexoses*, *heptoses*, *octoses*, etc. It is also obvious that only those compounds contain twice as many hydrogen atoms as oxygen atoms in which the number of oxygen and carbon atoms is equal, *i. e.*, those in which the valence corresponds to the number of carbon atoms—as the pentoses, $C_5H_{10}O_5$, and hexoses, $C_6H_{12}O_6$, whereas rhamnose (methyl pentose) has the formula $C_6H_{12}O_5$, and methyl hexose, the formula $C_7H_{14}O_6$.

1. GLUCOSES (MONOSES).

The glycoses, or glucoses, are mostly crystalline substances, very soluble in water, but dissolving with difficulty in alcohol. They possess a sweet taste. Their reducing power distinguishes them from other sweet-tasting, polyhydric alcohols, *e g.*, glycerol, erythrol and mannitol. This is in accord with their aldehyde or ketone character. The aldehyde alcohols, containing the atomic group—CH(OH).

CHO, are also known as *aldoses*, while the ketone alcohols—CO.CH_2.OH, have been called *ketoses*. The reducing properties of the latter correspond to those of acetyl carbinol, and the analogous α-ketols (p. 321).

(1) **Glycerose**, $C_3H_6O_3$, Triose, derived from glycerol, may be considered the lowest glucose. It consists of a mixture of glycerol aldehyde and dioxy-acetone, $CH_2(OH)$ CO.$CH_2(OH)$ (p. 454).

(2) **Erythrose**, $C_4H_8O_4$, Tetrose, from erythrol, probably represents a mixture of an aldose and a ketose.

(3) **Pentoses; Arabinose** and **Xylose**, $C_5H_{10}O_5$, and **Rhamnose**, $C_6H_{12}O_5$, methyl arabinose, belong to this class. They are aldoses or aldehyde derivatives of pentahydric alcohols, with which they are more fully discussed (p. 483). They manifest the general character of hexoses, in that they reduce Fehling's solution, yield osazones with phenylhydrazine, but cannot be fermented. They readily pass into furfurol when distilled with sulphuric and hydrochloric acids (*Berichte*, 23, 1751).

(4) **Hexoses.** These are the aldehyde or ketone derivatives of the hexahydric alcohols. Mannose, glucose and galactose are aldehyde derivatives. Fructose and probably sorbinose are ketoses. These compounds correspond to the formulas:—

$CH_2(OH).(CH.OH)_4.CHO$	and	$CH_2(OH).(CH.OH)_3.CO.CH_2(OH)$.
Glucose, Mannose, Galactose.		Fructose, Sorbinose.

This is evident from the conversion of the glucoses, by means of CNH, etc., into the corresponding hexa-oxy-carboxylic acids, and also by the reduction to heptylic acids. The first three yield normal heptylic acids, while fructose is converted into methyl-butyl acetic acid (pp. 495, 496). Bromine water, even in the cold, oxidizes the aldoses to their corresponding monocarboxylic acids (p. 489), whereas the ketoses (fructose and sorbinose) are not attacked (*Berichte*, 23, 2116).

Mannose, glucose, and galactose have the same structural formula, and are therefore (like the hexahydric alcohols, p. 486) alloisomeric or stereo-isomeric compounds. Mannose and fructose are derived from mannitol; galactose is the aldose of dulcitol, while glucose (grape sugar) probably corresponds to sorbite (p. 488). Further, mannose, glucose, and fructose, in accordance with the hypothesis of asymmetric carbon atoms (like mannitol, p. 487) exist in three optically different modifications—the dextro-, the lævo- and inactive forms.

In some reactions the glucoses behave differently from the aldehydes. Thus, they do not oxidize on exposure to the air, and do not react with fuchsine-sulphurous acid (p. 189). The penta-acetyl- and penta-benzoyl derivatives of dextrose and galactose do not manifest an aldehyde character (*Berichte*, 21, 2842; 22, Ref. 669). It has therefore been assumed that the hexoses possess a constitution similar to ethylene oxide or the lactones (*Berichte*, 22, 2211). However, it is hardly probable that this assumption is correct (*Berichte*, 21, 2841; 22, 2212; 23, 2117).

The hexoses occur frequently in plants, especially in ripe fruits. They are formed by the hydrolytic decomposition of all di- and poly-saccharides when they are boiled with dilute acids, or by ferments (p. 507). Mannose and fructose have been made artificially by oxidizing mannite. A more common method pursued in the formation of the glucoses is to reduce the monocarboxylic acids (their lactones) with sodium amalgam in acid solution (*Berichte*, 23, 930). Different hexoses have been directly synthesized by the condensation of formic aldehyde, CH_2O, acroleïn, C_3H_4O, and glyceric aldehyde, $C_3H_6O_3$:—

$$\underset{\substack{\text{Formic}\\ \text{Aldehyde.}}}{6CH_2O} = \underset{\text{Formose.}}{C_6H_{12}O_6} \qquad \underset{\substack{\text{Glyceric}\\ \text{Aldehyde.}}}{2C_3H_6O_3} = \underset{\text{Acrose.}}{C_6H_{12}O_6}.$$

E. Fischer (1890) effected the complete synthesis of grape sugar and fruit sugar by these methods.

Methylenitan was the first compound, resembling the sugars, that was prepared. Butlerow (1861) obtained it by condensing trioxymethylene (p. 192) with lime water. O. Loew (1885) obtained *formose* (*Jour. pr. Chemie*, 33, 321) in an analogous manner from oxymethylene, and somewhat later the fermentable *methose*, by the use of magnesia (*Berichte*, 22, 470, 478). E. Fischer considers these three compounds mixtures of different glucoses, among which α-acrose occurs (*Berichte*, 22, 360). The latter (together with β-acrose) is obtained by the action of barium hydroxide upon acroleïn bromide, $C_3H_5OBr_2$. This is probably because the glyceric aldehyde in it condenses (*Berichte*, 23, 389, 2131). By reduction with sodium amalgam α-acrose (identical with inactive fructose) passes into α-acrite, identical with inactive mannitol (p. 487). When the latter is oxidized it yields *i*-mannonic acid, which can be resolved into *d*- and *l* mannonic acid (p. 490). By reduction these acids are converted into *d*- and *l*-mannose. *d*-Mannose is changed through its osazone into *d*-fructose, *i. e.*, fruit sugar (p. 505) (E. Fischer, *Berichte*, 23, 373). *d*-Mannonic acid is converted into *d*-gluconic acid when heated, and by reduction with sodium amalgam the latter becomes *d*-glucose, *i. e.*, grape sugar (*Berichte*, 23, 799).

The hexoses show the ordinary *aldehyde reactions*:—

(1) By *reduction* they become hexahydric alcohols. Mannose and fructose yield mannitol, galactose yields dulcitol, and sorbite seems to result from the reduction of glucose (grape sugar).

(2) The *oxidation* of the hexoses does not occur directly upon exposure to the air. Oxidizing agents are necessary. Hence they show feeble *reducing* power. They precipitate the noble metals from solutions of their salts, and even reduce ammoniacal silver solutions in the cold. A very marked characteristic is their ability to precipitate cuprous oxide from warm alkaline cupric solutions (this is accelerated by tartaric acid). One molecule of hexose precipitates about five atoms of copper, as Cu_2O. This is

the basis of the volumetric method for the estimation of the glucoses by means of Fehling's solution. Maltose and milk sugar, of the di- and polysaccharides, only act directly upon the application of heat. The others must be first converted into glucoses (p. 508).

To prepare Fehling's solution, dissolve 34.65 grams of crystallized copper sulphate in water, then add 200 grams Rochelle salt and 600 c.cm of NaOH (sp. gr. 1.1200), and dilute the solution to 1 litre. 0.05 gram hexose is required to completely reduce 10 c.c. of this liquid. The end reaction is rather difficult to recognize, hence it is frequently recommended to estimate the separated cuprous oxide gravimetrically (*Berichte*, 13, 826; *Jour. pr. Chem.*, 21, 524). Consult *Berichte*, 23, 1035 for Soldaini's suggestion of using a copper carbonate solution for the estimation of the hexoses.

The hexoses are converted into their corresponding monocarboxylic acids (p. 488) by moderated oxidation with chlorine and bromine water, or silver oxide. More energetic oxidation changes them to saccharic and mucic acids. Milk sugar yields both acids at the same time. When boiled with dilute hydrochloric or sulphuric acid the hexoses, and apparently all the carbohydrates, sustain a gradual oxidation, the product being lævulinic acid, $C_5H_8O_3$ (p. 343) (*Berichte*, 21, 230).

When the glucoses are heated with dilute alkalies they turn brown, and pass into humus-like compounds. Saccharinic acids are produced when they are boiled with lime. The hexoses form tartaric acid chiefly when they reduce an alkaline copper solution.

In many reactions, for example, when heated alone or with sulphuric acid, we find that nearly all the carbohydrates yield traces of furfurol. This may be detected by the red coloration it yields with aniline (*Berichte*, 20, 541). The reaction of Molisch, for the detection of carbohydrates by means of α-naphthol and sulphuric acid (production of deep violet colors), is due to this compound (*Berichte*, 19, Ref. 746; 20, Ref. 517; 21, 2744).

(3) Being aldehydes or ketones the glucoses unite with hydrocyanic acid to form cyanhydrins. These yield the monocarboxylic acids. They combine with $H_2N.OH$ to form oximes. Only those of galactose and mannose have been isolated (*Berichte*, 20, 2673).

(4) The phenylhydrazine derivatives are especially interesting (pp. 191, 326). If one molecule of the phenylhydrazine (acetate) is allowed to act the first product will be a *hydrazone*, $C_6H_{12}O_5.(N.NH.C_6H_5)$. This class of compounds dissolves readily in water (with the exception of those derived from the mannoses and the higher glucoses, *Berichte*, 23, 2118). They generally crystallize from hot alcohol in colorless needles. Cold concentrated hydrochloric acid resolves them into their components.

Diphenylhydrazine, $H_2N.N(C_6H_5)_2$, often produces diphenyhydrazones, $C_6H_{12}O_5{:}N_2(C_6H_5)_2$ (*Berichte*, 23, 2619), that dissolve with difficulty.

In the presence of an excess of phenylhydrazine the hexoses, like all glucoses, combine with two molecules of it upon application of heat and form the *osazones* (E. Fischer):—

$$C_6H_{12}O_6 + 2H_2N.NH.C_6H_5 = C_6H_{10}O_4(N.NH.C_6H_5)_2 + 2H_2O + H_2.$$

Glucosazone.

The reaction is carried out by adding two parts of phenylhydrazine, two parts of 50% acetic acid, and about twenty parts of water to one part of glucose. This mixture is digested for about one hour upon the water bath. The osazone then separates in a crystalline form (*Berichte*, 17, 579; 20, 822; 23, 2117). In this reaction a hydrazone is first produced, and one of its alcohol groups, adjacent to either an aldehyde or ketone group, is oxidized to CO (inasmuch as two hydrogen atoms in the presence of phenylhydrazine produce aniline and ammonia), which then acts further upon a second molecule of phenylhydrazine. The same *glucosazone*, $CH_2(OH).(CH.OH)_3.C(N_5H.C_6H_5).CH(N_2H.C_6H_5)$ (see *Berichte*, 23, 2118), is thus obtained from mannose, glucose and fructose.

The osazones are yellow colored compounds (see tartrazine, p. 492). They are usually insoluble in water, dissolve with difficulty in alcohol, and crystallize quite readily. When glucosazone is reduced with zinc dust and acetic acid it becomes isoglucosamine (p. 505). Nitrous acid converts the latter into fructose (*Berichte*, 23, 2110). The reformation of the hexoses from their osazones is readily effected by digestion with concentrated hydrochloric acid; they are then resolved into phenylhydrazine and the *osones* (*Berichte*, 22, 88; 23, 2120):—

$$C_6H_{10}O_4(N_2H.C_6H_5)_2 + 2H_2O =$$

Glucosazone.

$$CH_2(OH).(CH.OH)_3.CO.COH + 2N_2H_3.C_6H_5.$$

Glucosone.

The osones dissolve readily in water, and have not been obtained free. They combine, like ketone-aldehydes, with two molecules of phenylhydrazine and form an osazone (p. 326). They are converted into glucoses by reduction (when digested with zinc dust and acetic acid). In this way fruit-sugar is prepared from glucosazone (*Berichte*, 23, 2121).

The osones yield quinoxalines with the orthodiamines. The glucoses also combine directly with the ortho-phenylenediamines (*Berichte*, 20, 281).

The *alcoholic* character of the hexoses is made manifest in the following reactions:—

1. The hydrogen of the hydroxyls can be readily replaced by acid radicals. The mixture of nitric and sulphuric acids (p. 454) converts them into esters of nitric acid—the nitro compounds (p. 514). The acetyl esters are best obtained by heating them with acetic anhydride and sodium acetate (or $ZnCl_2$). Five acetyl groups are thus introduced (*Berichte*, 22, 2207). The benzoyl esters are prepared with even less difficulty, it being only necessary to shake the hexoses with benzoyl chloride and caustic soda (p. 299). Pentabenzoyl derivatives are then formed (*Berichte*, 22, Ref. 668).

An elementary analysis will not yield a positive conclusion as to the number of acidyls that have entered compounds like those just mentioned. This is ascertained by first saponifying them with titrated alkali solutions, or better, with magnesia (*Berichte*, 12, 1531). Or, the acetic esters are decomposed by boiling them with dilute sulphuric acid. The acetic acid that distils over is then titrated (*Annalen*, 220, 217; *Berichte*, 23, 1442). The presence of hydroxyl in the glucoses may also be proved by means of phenylisocyanate, with which they form carbanilic esters (*Berichte*, 18, 2606).

Alkyl-sulphuric acids result upon treating the glucoses with chlorosulphonic acid, $ClHSO_3$. This is similar to the behavior of alcohols when exposed to like treatment (*Berichte*, 17, 2457). *Anilides* of the glucoses are formed when the latter are digested with the anilines. This is due to the replacement of a hydroxyl group (*Berichte*, 21, Ref. 399).

The *esters* of sugars with organic acids dó occur abundantly in plants and are termed *glucosides*. Thus, the tannins are glucosides of aromatic acids. All glucosides yield their components, when heated with acids or alkalies, or through the action of ferments.

The alcoholic hydrogen of the glucoses can also be replaced by bases, like CaO, BaO, and PbO, forming *saccharates*, which correspond to the alcoholates, and which are again decomposed by carbon dioxide.

The *hexoses* can be made to undergo fermentation quite readily when exposed to *schizomycetes*. They sustain various decompositions. The alcoholic fermentation is especially important. It is induced by yeast cells.

Alcoholic Fermentation.—This is induced by yeast, which is composed of microscopic (0.01 mm.) cells of *Saccharomyces cerevisiæ* and *vini*, which multiply during fermentation by budding. Alcoholic fermentation occurs at temperatures varying from 3–35° and is most rapid from 20–30°. Oxygen is requisite at the commencement, but it afterwards proceeds without air access. The hexoses mainly decompose, during fermentation, into alcohol and carbon dioxide: $C_6H_{12}O_6 = 2C_2H_6O + 2CO_2$. Glycerol (as much as 2.5 per cent.), succinic acid (0.6 per cent.), and fusel oils are formed simultaneously. The hexoses ferment directly; grape sugar somewhat more rapidly than fruit sugar. The disaccharates, $C_{12}H_{22}O_{11}$, are first decomposed by the soluble ferment of the yeast into hexoses; hence their fermentation proceeds very slowly and demands more yeast.

Other budding fungi, like *Mucor mucedo*, cause alcoholic fermentation. The fermentation phenomena occasioned by *schizomycetes* are exceedingly interesting. It is evident that the production of fusel oils in ordinary yeast fermentation (butyl and amyl alcohol) is due to these.

Alcoholic fermentation can occur unaccompanied by organisms in unimpaired, ripe fruits (grapes, cherries), providing the latter are exposed to an atmosphere of carbon dioxide.

In the *lactic acid* fermentation, the hexoses, milk sugar and gums decompose directly into lactic acid:—

$$C_6H_{12}O_6 = 2C_3H_6O_3.$$

The active agents are little, wand-like organisms (bacteria and micrococci). Decaying albuminous matter (decaying cheese) is requisite for their development, and it only proceeds in liquids which are not too acid (p. 357). The temperature most favorable varies from 30–50°. By prolonged fermentation the lactates suffer *butyric fermentation;* this is owing to the appearance of other bacilli (p. 226): $2C_3H_6O_3 = C_4H_8O_2 + 2CO_2 + 2H_2$.

In *mucous fermentation* chain-like cells (of 0.001 mm. diameter) appear. These convert grape sugar, with evolution of carbon dioxide, into a mucous, gummy substance; mannitol and lactic acid are formed at the same time.

Almost all the naturally occurring carbohydrates are *optically active,* as their solutions deviate the plane of polarization. Their specific rotatory power (p. 62) is not only governed by temperature and the concentration of their solutions, but is also very frequently influenced by the presence of inactive substances (*Berichte*, 21, 2586 and 2599). Further, some substances show the phenomena of bi-rotation and semi-rotation. Brief heating of their solutions will usually bring about a recurrence of constant rotation. The determination of the rotatory power of the carbohydrates by means of the saccharimeter serves to ascertain their purity and is frequently applied in estimating their percentage content—*optical sugar test.*

1. **Mannose,** $C_6H_{12}O_6$, is the aldehyde of mannitol. Like the latter, it exists in three forms (p. 487): dextro-, lævo- and inactive mannose.

d-Mannose was first prepared by oxidizing ordinary *d*-mannitol (together with *d*-fructose) with platinum black or nitric acid (*Berichte*, 22, 365). It is also obtained from salep mucus (*Annalen*, 249, 251; *Berichte*, 21, 2150), and most easily from seminine (reserve-cellulose), occurring in different plant seeds, when this is boiled with dilute sulphuric acid (hence called *seminose*) (*Berichte*, 22, 609, 3218). *d*-Mannonic acid yields it upon reduction. It is an amorphous mass. very soluble in water, and dextro-rotatory. It reduces Fehling's solution, and is fermented by yeast (*Berichte*, 22, 3224). Its *hydrazone* dissolves with difficulty in water, and forms brilliant leaflets, that melt at 195°. Its *osazone*, $C_6H_{10}O_4(N_2H.C_6H_5)_2$, is identical with *d*-glucosazone. Nascent hydrogen converts it into *d*-mannitol. Bromine oxidizes it to *d*-mannonic acid. Hydrocyanic acid causes it to pass into *d*-mannoheptonic acid (p. 495).

l-**Mannose** results when *l*-mannonic acid is reduced (p. 490, *Berichte*, 23, 373). It is very similar to the preceding compound, but is lævo-rotatory, and is fermented with more difficulty. Its *hydrazone* also dissolves with difficulty, and melts at 195°. It unites with two molecules of phenylhydrazine to form *l*-glucosazone (see below). It becomes *l*-mannitol by reduction.

i-**Mannose** is formed by the reduction of inactive mannonic acid. It is quite similar to the two preceding compounds, but is inactive. Its *hydrazone* dissolves with difficulty, melts at 195°, and is inactive. Its osazone is *i*-glucosazone. Yeast decomposes it, the *d*-mannose is fermented, and *l*-mannose remains (*Berichte*, 23, 382).

2. **Glucose,** $C_6H_{12}O_6$, is probably the aldehyde of sorbite, and occurs as dextro- lævo- and inactive glucose (p. 498).

d-**Glucose,** or *Grape Sugar,* formerly called *dextrose,* occurs (always with fruit sugar) in many sweet fruits and in honey; also in the urine in *Diabetes mellitus.* It is formed by the hydrolytic decomposition of poly-saccharides (cane sugar, starch, cellulose) and glucosides. It is prepared on a large scale by boiling starch with dilute sulphuric acid (see *Berichte*, 13, 1761). *The synthesis of grape sugar has been made possible by the production of glucose in the reduction of d-gluconic acid* (p. 499).

Commercial grape sugar is an amorphous, compact mass, containing only about 60 per cent. glucose, along with a dextrine-like substance (gallesine, $C_{12}H_{24}O_{10}$), which is not fermentable (*Berichte*, 17, 2456). Pure grape sugar, with one molecule of water, can be prepared from this, by crystal ization from alcohol.

The best method for preparing pure crystallized grape sugar consists in adding to 80 per cent. alcohol, mixed with $\frac{1}{15}$ volume fuming hydrochloric acid, finely pulverized cane sugar, as long as the latter dissolves on shaking (*Journ. prakt. Chem.*, 20, 244).

Grape sugar crystallizes from water at the ordinary temperature, or dilute alcohol, with one molecule of water, in nodular masses, melting at 86°; at 110° it loses its water of crystallization. At 30–35° it crystallizes from its concentrated aqueous solution, and from its solution in ethyl or methyl alcohol, in anhydrous, hard crusts, melting at 146° (*Berichte*, 15, 1105).

Grape sugar is not quite so sweet to the taste as cane sugar, and serves to doctor wines.

Aqueous grape sugar is dextro-rotatory $[\alpha]_D = 52.6°$, and exhibits *bi-rotatory* power, *i. e*, the freshly prepared solution deviates the polarized ray almost twice as strongly as it does after standing some time. At ordinary temperatures the deviation does not become constant until the expiration of twenty-four hours, whereas when boiled it does so in the course of a few minutes. Furthermore, the specific rotation of dextrose is appreciably augmented by concentration (*Berichte*, 17, 2234). This is dependent upon the decomposition of more complex crystal-molecules into normal molecules. This has been proved by determining the molecular weight by the method of Raoult (*Berichte*, 21, Ref 505).

With baryta and lime grape sugar forms saccharates, like $C_6H_{12}O_6.CaO$, and $C_6H_{12}O_6.BaO$. These are precipitated by alcohol. With NaCl it forms large crystals, $2C_6H_{12}O_6.NaCl + H_2O$, which sometimes separate in the evaporation of diabetic urine.

When grape sugar and acetyl chloride are heated, so-called *aceto-chlorhydrose*, $C_6H_7O\left\{\begin{array}{l}Cl\\(O.C_2H_3O)_4\end{array}\right.$, results. This has been used in the synthesis of the disaccharates.

Grape sugar exhibits all the properties of the aldoses (p. 498). Its *phenylhydrazone* is very soluble and melts at 145°.*

d-Glucosazone, its osazone, consists of yellow needles, melting at 204–205° to a red liquid. Its aqueous solution is lævo-rotatory.

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* Skraup (*Berichte*, 22, Ref. 669) maintains that grape sugar forms two hydrazones with phenylhydrazine, the one melting at 143°, and the other at 116°.

It may also be prepared from *d*-mannose and *d*-fructose, as well as from glucosamine and isoglucosamine. Invert sugar is best adapted for the preparation of *d*-glucosazone (see below, *Berichte*, **19**, 1921). Concentrated hydrochloric acid converts *d*-glucosazone into phenylhydrazine and *glucosone*, $C_6H_{10}O_6$ (p. 501); which regenerates *d*-glucosazone with two molecules of phenylhydrazine. It is a non-fermentable liquid, and if it be reduced with zinc and acetic anhydride, is converted into fruit sugar (= *d*-fructose) (*Berichte*, **22**, 88).

The following are derivatives of grape sugar:—

Isoglucosamine, $C_6H_{13}NO_5 = CH_2(OH)(CH.OH)_3.CO.CH_2.NH_2$, is formed by reducing glucosazone with zinc dust and acetic acid. It reduces alkaline copper solutions, combines with phenylhydrazine to re form *d* glucosazone and is converted by nitrous acid into fruit sugar (*Berichte*, **23**, 2120).

Glucosamine, $C_6H_{13}NO_5$, is produced on warming chitine (found in lobster shells) with concentrated HCl (*Berichte*, **17**, 243). Free glucosamine separates from alcohol in needles. Nitric acid oxidizes it to isosaccharic acid. It forms glucosazone with phenylhydrazine.

l-**Glucose,** $C_6H_{12}O_6$, is formed when the lactone of *l*-gluconic acid (p. 490) is reduced with sodium amalgam. It is perfectly similar to grape sugar. It melts at 143°, but is lævo-rotatory, $[\alpha]_D = -51.4°$. Its glucosazone is, however, dextrorotatory. Its *diphenylhydrazone*, $C_6H_{10}O_5{:}N.N(C_6H_5)_2$, dissolves with difficulty, and melts at 163° (*Berichte*, **23**, 2618).

i-**Glucose,** $C_6H_{12}O_6$, results from the union of *d*- and *l*-glucose, and by the reduction of *i*-gluconic lactone. Phenylhydrazine converts it into *i-glucosazone*, $C_6H_{10}O_5(N_2H.C_6H_5)_2$. This may also be obtained from *i*-mannose. It crystallizes in yellow needles, melting at 217-218°. The same *i*-glucosazone is produced from synthetic *α*-acrose (fructose), *d*-mannose, *d* glucose and *d*-fructose (fruit-sugar) (*Berichte*, **23**, 383, 2620). Inactive fructose is formed when *i*-glucosazone is decomposed with hydrochloric acid, and by the reduction of the *i*-glucosone, first formed, with zinc dust and acetic acid. Diphenylhydrazine and *i*-glucose yield a diphenylhydrazone, crystallizing in leaflets, melting at 133°. *i*-Glucose is fermented by yeast. *l*-Glucose remains behind.

3. **Fruit Sugar,** $C_6H_{12}O_6$, is the ketone derivative (the ketose) of mannitol. It occurs as dextro-, lævo- and inactive fruit sugar (p. 498).

d-**Fructose,** or **Fruit Sugar,** formerly called *lævulose*, is found in almost all sweet fruits, together with an equal amount of grape sugar. It is likely that cane sugar first forms in the plants and that a ferment at once breaks it up into grape sugar and fruit sugar. It is formed, together with grape sugar, in the so-called *inversion*, or decomposition of cane sugar, by boiling with acids or by the action of ferments. The mixture of the two is called *invert sugar*. The decomposition of inosite yields fruit sugar. It is artificially prepared (together with *d*-mannose) by oxidizing *d*-mannitol, as well as from *d*-glucosazone and isoglucosamine. *In this way the complete synthesis of fruit sugar has been effected* (p. 499).

Preparation.—Mix 10 parts invert sugar with 6 parts calcium hydroxide and 50 parts of water. On pressing the moist mass, the liquid lime compound of dextrose is removed and the residual solid is the lime compound of lævulose. This is decomposed by oxalic acid, the lime oxalate filtered off, and the solution evaporated (*Berichte*, 14, 2418).

A much simpler method is to heat inuline, with water, to 100° for twenty-four hours, when it is completely changed to lævulose (*Annalen*, 205, 162; *Berichte*, 23, 2107).

Fruit sugar forms a thick syrup which at 100° dries to a gummy, deliquescent mass. When the syrup is repeatedly extracted with cold absolute alcohol, the lævulose gradually crystallizes out in fine, silky needles, which fuse at 95° and lose water at 100°. It is more readily soluble in water and alcohol than grape sugar, and rotates the plane to the left more powerfully than the latter. Its specific rotatory power in 20 per cent. solution is $[\alpha]_D = -71.4°$ at 20° (*Berichte*, 19, 393). Consequently invert sugar (grape sugar and fruit sugar) is lævo-rotatory. Fruit sugar is more slowly fermented by yeast than grape sugar; therefore in the fermentation of invert sugar the solution finally contains only fruit sugar.

In all reactions fruit sugar closely resembles grape sugar, and reduces an alkaline copper solution in the same proportion as the latter. It is converted into *d*-mannitol by sodium amalgam. It yields the same *d*-glucosazone with phenylhydrazine. However, in oxidations it sustains, owing to its ketone character, more complete decompositions, resulting in the production of gluconic and tartaric acids. Hydrochloric and hydrocyanic acids convert it into fructose-carboxylic acid, which may be reduced to methylbutyl acetic acid (p. 496).

l-**Fructose**, $C_6H_{12}O_6$, is produced by fermenting inactive fructose (*a*-acrose) with yeast; the *d*-fructose being destroyed. It has not been isolated, but yet forms *l*-glucosazone (p. 505) with phenylhydrazine (*Berichte*, 23, 389).

i-**Fructose**, inactive lævulose, is probably identical with synthetic *a-acrose.* Sodium amalgam converts it into *a-acrite*, identical with *i* mannitol (p. 487). Yeast breaks it up, leaving *l*-fructose. Its *osazone* is identical with *i*-glucosazone, from which *i*-fructose can again be regenerated. *a*-Acrite can also yield *i*-mannonic acid, and the latter fruit sugar and grape sugar.

4. **Galactose**, $C_6H_{12}O_6$, **Lactose**, is the aldose of dulcitol (p. 488). It is formed on boiling milk sugar with dilute acids, and is obtained from such gums (called galactans) (*Berichte*, 20, 1003), as yield much mucic acid when oxidized. To prepare it boil milk sugar with dilute sulphuric acid (*Annalen*, 227, 224). It crystallizes in nodules of grouped needles or leaflets, which melt at 166°; it dissolves with much more difficulty in water than *d*-glucose. Its solution is dextrorotatory. It readily reduces alkaline copper solutions and is fermentable with yeast (*Berichte*, 21, 1573). Nitric acid oxidizes it to mucic acid, bromine to galactonic acid (p. 491) and sodium amalgam converts it into dulcitol. Hydrocyanic and hydrochloric acids convert it into galactose-carboxylic acid. Phenylhydrazine converts galactose into a *hydrazone*, $C_6H_{12}O_5{:}N_2H.C_6H_5$, melting at 158°, and *galactosazone*, $C_6H_{10}O_4.(N_2H.C_6H_5)_2$, melting at 193°.

5. **Sorbinose, Sorbine**, $C_6H_{12}O_6$, a ketone alcohol (ketose), is found in mountain-ash berries, and consists of large crystals, which possess a very sweet taste. It reduces alkaline copper solutions, but is incapable of fermentation under

the influence of yeast. Oxidized with nitric acid it yields trioxyglutaric acid (*Berichte*, 21, 3276). Its osazone, *sorbinosazone*, melts at 164°.

6. **Methyl Hexose,** $C_7H_{14}O_6 = C_6H_{11}(CH_3)O_6$, rhamno-hexose, is produced in the reduction of rhamnose-carboxylic acid (p. 491). It crystallizes quite readily from alcohol and melts at 181°. Its osazone melts near 200° (*Berichte*, 23, 936). Hydrocyanic acid and hydrochloric acid convert it into methylheptonic acid. This yields methylheptone by reduction.

(5) **Heptoses,** $C_7H_{14}O_7$.

These compounds are synthetically prepared by reducing the corresponding heptonic acids, $C_7H_{14}O_8$ (their lactones), with sodium amalgam. In their properties they are very similar to the hexoses. They are not fermented by yeast (*Berichte*, 23, 935).

d-**Manno-heptose,** $C_7H_{14}O_7$, is obtained from mannoheptonic acid (*Berichte*, 23, 2228). Perseïte yields it when oxidized (p. 494). It crystallizes in needles melting at 135°. Its *hydrazone*, $C_7H_{14}O_6(N_2H.C_6H_5)$, dissolves with difficulty and melts about 198°. Its *osazone*, $C_7H_{12}O_5(N_2H.C_6H_5)_2$, melts near 200°. Sodium amalgam converts it into perseïte (p. 494). Manno-octonic acid, $C_8H_{16}O_9$, is obtained upon treating it with hydrocyanic and hydrochloric acids (*Berichte*, 23, 2233).

d-**Gluco-heptose,** $C_7H_{14}O_7$, from gluco-heptonic acid, crystallizes in beautiful plates, melting at 190°. Its hydrazone is very soluble. Its *osazone* melts at 197°. Hydrocyanic acid and hydrochloric acid convert it into gluco-octonic acid.

Gala-heptose, $C_7H_{14}O_7$, from galaheptonic acid, forms a hydrazone that dissolves with difficulty. Its osazone melts about 220°.

Methyl Heptose, $C_8H_{16}O_7 = C_7H_3(CH_3)O_7$, *rhamno-heptose*, is derived from methyl heptonic acid. Its hydrazone dissolves with difficulty.

(6) **Octoses,** $C_8H_{16}O_8$ **and Nonoses,** $C_9H_{18}O_9$. The octoses are derived from the heptose-carboxylic acids.

d-**Manno-octose,** $C_8H_{16}O_8$, from manno-octonic acid (p. 496), is syrup-like, but yields a beautiful hydrazone and osazone. Sodium amalgam converts it into *d*-manno-octite, $C_8H_{18}O_8$ (*Berichte*, 23, 2234). Prussic and hydrochloric acids convert it into *d*-manno-nononic acid, $C_9H_{18}O_{10}$ (p. 496). By reduction the latter yields

d-**Manno-nonose,** $C_9H_{18}O_9$. This is very similar to grape sugar. It ferments under the influence of yeast. The heptoses and octoses do not ferment. The hydrazone melts at 223°, the osazone about 217° (*Berichte*, 23, 2237).

2. DISACCHARIDES.

Only the disaccharides of the hexoses, $C_6H_{12}O_6$, are known. They consist of two molecules of the glucoses or monoses (p. 497), and therefore are called *bioses*. Their formula would therefore be $C_{12}H_{22}O_{11}$. By the absorption of water—by hydrolysis—they are resolved into two molecules of the hexoses:—

$$C_{12}H_{12}O_{11} + H_2O = 2C_6H_{12}O_6.$$

Thus cane sugar decomposes into grape-sugar (*d*-glucose) and fruit-sugar (*d*-fructose), milk sugar into *d*-glucose and galactose, maltose into two molecules of *d*-glucose, etc., etc., etc.

When the di- and poly-saccharides are heated with water and a little acid they undergo hydrolysis. Its rapidity, according to Ostwald, bears a close relation to the affinity of the acids (*Jour. pr. Chem.* (2), 31, 307). The action of various unorganized *ferments*, such as *diastase* and *synaptase* or *emulsin* (contained in sweet and bitter almonds), upon the saccharides produces a similar decomposition. Invertin (the ferment of yeast), ptyalin (the ferment of saliva), trypsin, pepsin, and other animal secretions exert a like action. Thus, yeast resolves cane sugar into grape sugar and fruit sugar, and starch into dextrine and maltose.

Formerly the decomposition of cane sugar was termed *inversion*, because the optical rotation was reversed (owing to the stronger lævo-deviation of the plane by the fruit sugar). The product (a mixture of dextrose and lævulose) is *invert sugar* (p. 505).

Prolonged heating with acids causes *reversion;* the glucoses (especially fructose) undergo a retrogressive condensation to dextrine-like substances (*Berichte*, 23, 2094).

The constitution of the disaccharides indicates that they are ether-like anhydrides of the hexoses. The union is effected through the alcohol or aldehyde groups. Milk sugar and maltose also contain the aldose group, CH(OH).CHO, because they reduce Fehling's solution upon boiling, form osazones with phenylhydrazine, and when oxidized with bromine water yield monobasic acids, $C_{12}H_{22}O_{12}$, lacto- and malto-bionic acid (p. 510) (*Berichte*, **21**, 2633; **22**, 361).

Cane sugar does not show reducing power and does not yield an osazone. The reducing groups (of grape sugar and fruit sugar) appear to be combined in this compound. It is consequently not capable of direct fermentation with yeast. Inversion must first take place. Maltose is fermented quite readily, while milk sugar ferments with difficulty. After inversion cane sugar forms the same glucosazone as grape sugar and fruit sugar.

Cane Sugar, $C_{12}H_{22}O_{11} = C_{12}H_{14}O_3(OH)_8$, Saccharose, occurs in the juice of many plants, chiefly in sugar cane, in some varieties of maple and in beet-roots (10–20 per cent.) from which it is prepared on a commercial scale. While the hexoses occur mainly in fruits, cane sugar is usually contained in the stalks of plants.

Its commercial manufacture from cane or beet sugar is, from a chemical point of view, very simple. The sap obtained by pressing or diffusion is boiled with milk of lime, to saturate the acids, and precipitate the albuminoid substances. The juice is next saturated with carbon dioxide, filtered through animal charcoal, concentrated in a Roberts' Machine, and further evaporated in *vacuum pans* to a thick syrup, out of which the solid sugar separates on cooling. The raw sugar obtained in this manner is further purified with a pure sugar solution, in the centrifugal machine, etc.—*refined sugar.*

The syrupy mother liquor from the sugar is called molasses; it contains upwards of 50 per cent. of cane sugar which is prevented from crystallizing by the presence of salts and other substances. It is either converted into alcohol or the cane-sugar is extracted from it by the fermenting process. The sparingly soluble saccharates of lime and strontium are obtained from the molasses (see below) and these are freed from impurities by washing with water or dilute alcohol. The purified saccharates are afterwards decomposed by carbon dioxide, and the juice which is then obtained, after the above plan, is further worked up.

When its solutions are evaporated slowly cane sugar separates in large monoclinic prisms and dissolves in ⅓ part water of medium temperature; it dissolves with difficulty in alcohol. Its sp. gr. equals 1.606. Its aqueous solution is lævo-rotatory; the influence of concentration upon the specific rotation is slight; it, however, diminishes (opposite of grape sugar) with increased concentration. Its real rotatory power, A_D, at 20° is + 64.1 (p. 62). Cane sugar melts at 160° and on cooling solidifies to an amorphous glassy mass; in time this again becomes crystalline and non-transparent. At 190–200° it changes to a brown non-crystallizable mass, called *Caramel*, which finds application in coloring liquors.

Cane sugar decomposes into dextrose and lævulose (invert sugar) when boiled with dilute acids. Mixed with concentrated sulphuric acid it is converted into a black, humus-like body. Sacccharic acid, inactive tartaric acid and oxalic acid are formed when it is boiled with nitric acid.

Cane sugar yields saccharates (p. 502) with the bases. An aqueous sugar solution readily dissolves lime. If finely divided burnt lime (CaO) (1 molecule to 1 molecule sugar) be dissolved in a dilute sugar solution (6–12 per cent.) alcohol will precipitate the *monobasic saccharate*, $C_{12}H_{22}O_{11}.CaO + 2H_2O$, which, when deprived of its water at 100°, is a white amorphous mass, that is quite soluble in cold water. Two molecules of CaO afford $C_{12}H_{22}O_{11}.2CaO$, which separates, in the cold, in beautiful crystals. If CaO be added to its solution at temperatures below 35°, all the sugar will be precipitated as tribasic saccharate, $C_{12}H_{22}O_{11}.3CaO$; this is not readily soluble in water. Upon the above deportment is based C. Steffen's substitution process, by which sugar is separated from molasses (*Berichte*, 16, 2764). Strontium and barium give perfectly similar saccharates (*Berichte*, 16, 984). On boiling the sugar solution with lead oxide we get $C_{12}H_{18}Pb_2O_{11}$.

Cane sugar heated to 160° with an excess of acetic anhydride gives *octacetyl ester*, $C_{12}H_{14}O_3(O.C_2H_3O)_8$; this is a white mass, insoluble in water and acetic acid. The action of concentrated nitric acid and sulphuric acid yields the tetranitrate, $C_{12}H_{18}(NO_2)_4O_{11}$, a white mass; it explodes violently.

Milk Sugar, $C_{12}H_{22}O_{11} + H_2O$, **Lactose,** has thus far been found in the animal kingdom only, and occurs in the milk of mammals, in the amniotic liquor of cows, and in certain pathological secretions.

Milk sugar is prepared from whey. This is evaporated to the point of crystallization and the sugar which separates purified by repeated crystallization.

Milk sugar crystallizes in white, hard, rhombic prisms, containing one molecule of water. It is soluble in 6 parts cold or 2½ parts hot water, has a faint sweet taste, and is insoluble in alcohol.

Its aqueous solution is dextro-rotatory and exhibits *bi-rotation* (p. 504). When the constant rotatory point is obtained by heating, the specific rotatory power will vary considerably with the concentration. Milk sugar loses its water of crystallization at 140°, chars, melts at 205°, and suffers further decomposition. It resembles the hexoses in reducing ammonical silver solutions; this it effects even in the cold, but in case of alkaline copper solutions boiling is necessary to reach the desired end. Milk sugar yields galactose and *d*-glucose when it is heated with dilute acids; it ferments with difficulty with yeast, but undergoes the *lactic* fermentation with great readiness. Nitric acid oxidizes it to saccharic acid, mucic acid and additional oxidation products.

Bromine water converts it into lactobionic acid, $C_{12}H_{22}O_{12}$, which is changed to gluconic acid and galactose upon digesting it with acids (*Berichte*, **22**, 361).

An octacetyl ester is obtained by treating the acid with acetic anhydride. A so-called nitro-lactose, $C_{12}H_{17}(NO_2)_5O_{11}$, crystallizes from alcohol in leaflets. This melts at 139° and explodes at 155°.

It unites with phenylhydrazine and forms *phenyl-lactosazone*, $C_{12}H_{20}O_9.(N_2H.C_6H_5)_2$, that melts at 200° (*Berichte*, **20**, 829).

Maltose, $C_{12}H_{22}O_{11} + H_2O$, is a variety of sugar formed, together with dextrine, by the action of malt diastase (p. 508) upon starch (in the mash of whiskey and beer). It is capable of direct fermentation. It was formerly supposed to be grape sugar. It is also an intermediate product in the action of dilute sulphuric acid upon starch, and of ferments (diastase, saliva, pancreas) upon glycogen (p. 513).

In the normal sugaring of pasty starch by diastase, at a temperature of 50–63°, nearly ⅔ maltose and ⅓ dextrine are produced:—

$$\underset{\text{Starch.}}{3C_6H_{10}O_5} + H_2O = \underset{\text{Maltose.}}{C_{12}H_{22}O_{11}} + \underset{\text{Dextrine.}}{C_6H_{10}O_5}.$$

The quantity of maltose produced at more elevated temperatures (above 63°) steadily diminishes up to 75° when the action of diastase ceases (*Berichte*, **12**, 949). These conditions are important in the manufacture of rum and the brewing of beer. In the first case the mash obtained by the production of sugar at 60° is cooled, then the maltose at once ferments and dextrine in consequence of the after-action of the diastase, is first converted into grape sugar and then fermented; therefore, the fermentation of starch is almost a perfect one. In beer-brewing the mash is boiled, to destroy the diastase, so that by the action of ferments only the maltose suffers fermentation; dextrine remains unaltered.

In preparing maltose, starch paste made by boiling with water is converted, at 60°, into sugar, by diastase, the solution then boiled, the filtrate concentrated to a syrup and the maltose extracted by strong alcohol (*Annalen*, **220**, 209).

Maltose is usually obtained in the form of crystalline crusts, composed of hard, white needles, that lose their water of crystallization at 100°. In properties it closely approaches grape sugar. It is directly fermented by yeast and reduces an alkaline copper solution, but to only about ⅔ the amount effected by grape sugar; 100 parts maltose, judging from its reducing power, are equivalent to 61 parts grape sugar, but in the case of Fehling's solution diluted four times, they correspond to about 66.8 parts of the second (*Annalen*, **220**, 220). Its rotatory power is but slightly influenced by the temperature and concentration of the solution, $[\alpha]_D = +140.6°$ (*Annalen*, **220**, 200).

Diastase does not exert any further change upon maltose; when boiled with dilute acids, it passes completely into grape sugar. Nitric acid oxidizes it to saccharic acid, while chlorine changes it to malto-bionic acid, $C_{12}H_{22}O_{12}$. This yields grape sugar and gluconic acid when it is heated with acids. Maltose and milk sugar very probably possess the same structural formula (*Berichte*, **22**, 1941).

When heated with sodium acetate and acetic anhydride, it yields *octoacet-maltose*, $C_{12}H_{14}(C_2H_3O)_8O_{11}$, which melts at 150-155°.

When boiled with lime water, it forms isosaccharin (p. 484). Phenylhydrazine converts it into phenylmaltosazone, $C_{12}H_{20}O_9(N_2H.C_6H_5)_2$, melting at 82°.

Mycose, $C_{12}H_{22}O_{11} + 2H_2O$, Trehalose, occurs in several species of fungi, in ergot of rye, and in the oriental *Trehala*. It is distinguished from cane sugar by its ready solubility in alcohol, greater stability and stronger rotatory power.

Melebiose, $C_{12}H_{22}O_{11}$, is produced, together with *d*-fructose, in the hydrolysis of meletriose. Its osazone, $C_{12}H_{20}O_9.(N_2H.C_6H_5)_2$, is soluble. Further hydrolysis converts it into *d*-glucose and galactose (*Berichte*, **22**, 3119; **23**, 1438).

Raffinose and melezitose are *Trisaccharides*.

Melitose, Raffinose, $C_{18}H_{32}O_{16} + 5H_2O$, Melitriose. It occurs in rather large quantity in Australian manna (varieties of Eucalyptus), in the flour of cotton seeds, in small amounts in sugar beets, and being more soluble than cane sugar, it accumulates in the molasses in the sugar manufacture. From this it crystallizes out with the sugar. Its crystals have peculiar terminal points, and show strong rotatory power (Plus sugar).

Raffinose is obtained from molasses, or by treating plus sugar with alcohol, in which the raffinose dissolves with more difficulty than the sugar (*Annalen*, **232**, 173). To determine the raffinose in the molasses and tailings, extract it with methyl alcohol (*Berichte*, **19**, 2872), then polarize and invert, or determine the amount of mucic acid obtained by oxidizing the raffinose with HNO_3 (*Berichte*, **19**, 3116).

It crystallizes in needles, more soluble in water and less in alcohol than cane sugar. It dissolves quite readily in methyl alcohol. It loses its water of crystallization in a vacuum and when warmed. It is more strongly dextro-rotatory than cane sugar: $(\alpha)_D = 104°$. It does not reduce Fehling's solution, but is easily fermented by yeast.

By hydrolysis it yields fructose and melibiose (*Berichte*, **23**, Ref. 103). The determination of its molecular weight by the method of Raoult showed it to be a triose (*Berichte*, **21**, 1569).

Melezitose, $C_{18}H_{32}O_{16} + 2H_2O$, occurs in the juice of *Pinus Larix*, and resembles cane sugar very much. It is distinguished from the latter by its greater rotatory power and in not being so sweet to the taste. It melts at 148° when anhydrous. It is also a triose (*Berichte*, **22**, Ref. 759).

3. POLYSACCHARIDES.

It is very probable that the polysaccharides having the empirical formula $C_6H_{10}O_5$, really possess a much higher molecular weight, $(C_6H_{10}O_5)_n$. They differ much more from the hexoses than the di- and tri-saccharides. They are, as a general thing, amorphous, dissolve with difficulty in water, and lack most of the chemical characteristics of the hexoses. By hydrolysis, that is when boiling them with dilute acids, or under the influence of ferments (p. 508), nearly all are finally broken up into their component hexoses (see dextrine). Their alcoholic nature is shown in their ability to form acetyl and nitric esters.

Starch, Amylum, $(C_6H_{10}O_5)_n$ or $C_{36}H_{62}O_{31}$ (p. 497), is found in the cells of many plants, in the form of circular or elongated microscopic granules, having an organized structure. The size of the granules varies, in different plants, from 0.002–0.185 mm. Air dried starch contains 10–20 per cent. of water; dried over sulphuric acid it retains some water which is only removed at 100°. Starch granules are insoluble in cold water and alcohol. When heated with water they swell up at 50°, burst, partially dissolve and form *starch paste*, which turns the plane of polarization to the right. The soluble portion is called *granulose*, the insoluble, *starch cellulose*. Alcohol precipitates a white powder—*soluble starch*—from the aqueous solution. The blue coloration produced by iodine is characteristic of starch, both the soluble variety and that contained in the granules (*Berichte*, 20, 694). Heat discharges the coloration, but it reappears on cooling.

Boiling dilute acids convert starch into dextrine and *d*-glucose. When heated from 160–200° it changes to dextrine. Malt diastase changes it to dextrine and maltose.

Concentrated sulphuric acid combines with starch, yielding a compound which forms salts with bases. Heated with acetic acid we get the *triacetyl derivative*, $C_6H_7O_2(O\,C_2H_3O)_3$, an amorphous mass, which regenerates starch when treated with alkalies. Concentrated nitric acid produces nitrates.

Other starch-like compounds are:—

Paramylum, $C_6H_{10}O_5$, which occurs in form of white grains in the infusoria *Euglena viridis*. It resembles common starch, but is not colored by iodine, and is soluble in potassium hydroxide.

Lichenine, $C_6H_{10}O_5$, moss-starch, occurs in many lichens, and in Iceland moss (*Cetraria islandica*), from which it may be extracted by water. The solution becomes gelatinous, dries to a hard mass, and on treatment with boiling water again forms a jelly. Iodine imparts a dirty blue color to it. It yields dextrose when boiled with dilute acids.

Inulin is found in the roots of dahlia, in chicory, and in many Compositæ (like *Inula Helenium*); it is a white powder which dissolves in boiling water, forming a clear solution. Iodine gives it a yellow color. When boiled with water it is completely changed to fruit sugar.

Glycogen, $C_6H_{10}O_5$, animal starch, occurs in the liver of mammals and is a mealy powder, which is precipitated from solution by alcohol; it forms a paste with cold water, and on heating is dissolved in it. Iodine imparts a reddish-brown color to it. Boiling with dilute acids causes it to revert to dextrose, and ferments change it to maltose.

The Gums, $(C_6H_{10}O_5)_n$. These are amorphous, transparent substances widely disseminated in plants; they form sticky masses with water and are precipitated by alcohol. They are odorless and tasteless. Some of them yield clear solutions with water, while others swell up in that menstruum and will not filter through paper. The first are called the *real gums* and the second *vegetable mucilages*. Nitric acid oxidizes them to mucic and oxalic acids.

Dextrine. By this name are understood substances, readily soluble in water and precipitated by alcohol; they appear as by-products in the conversion of starch into dextrine, *e.g.*, heating starch alone from 170–200°, or by heating it with dilute sulphuric acid. Different modifications arise in this treatment; amylodextrine, erythrodextrine, achrodextrine; they have received little study. They are gummy, amorphous masses, whose aqueous solutions are dextro-rotatory, hence the name dextrine. They do not reduce Fehling's solution, even on boiling, and are incapable of direct fermentation; in the presence of diastase, however, they can be fermented by yeast (p. 510). They are then converted into *d*-glucose. They yield the same product when boiled with dilute acids.

Dextrine is prepared commercially by moistening starch with two per cent. nitric acid, allowing it to dry in the air, and then heating it to 110°. It is employed as a substitute for gum (*Berichte*, 23, 2104).

Arabin exudes from many plants, and solidifies to a transparent, glassy, amorphous mass, which dissolves in water to a clear solution. Gum arabic or gum Senegal consists of the potassium and calcium salts of arabic acid. The latter can be obtained pure by adding hydrochloric acid and alcohol to the solution. It is then precipitated as a white, amorphous mass, which becomes glassy at 100°, and possesses the composition $(C_6H_{10}O_5)_2 + H_2O$. It forms compounds with nearly all the bases; these dissolve readily in water.

Some gum varieties, *e.g.*, gum-arabic, yield galactose in considerable quantity when boiled with dilute sulphuric acid; and with nitric acid they are converted into mucic acid; others (like cherry gum) are transformed on boiling with sulphuric acid into arabinose, $C_5H_{10}O_5$ (p. 483), and into oxalic acid, not mucic acid, by nitric acid. The gum, extracted from beechwood by alkalies and precipitation with acids, is converted into xylose (p. 483) by hydrolytic decomposition.

Bassorin, vegetable gum, constitutes the chief ingredient of gum tragacanth, Bassora gum, and of cherry and plum gums (which last also contain arabin). It swells up in water, forming a mucilaginous liquid, which cannot be filtered; it dissolves very readily in alkalies.

Cellulose, $C_{12}H_{20}O_{10}$, wood fibre, lignose, forms the principal ingredient of the cell membranes of all plants, and exhibits an organized structure. To obtain it pure, plant fibre, or better, wadding, is treated successively with dilute potash, dilute hydrochloric acid, water, alcohol and ether, to remove all admixtures (incrusting substances). Cellulose remains then as a white, amorphous mass. Fine, so-called Swedish, filter paper consists almost entirely of pure cellulose.

Cellulose is insoluble in most of the usual solvents, but dissolves without change in an ammoniacal copper solution. Acids, various salts of the alkalies and sugar precipitate it as a gelatinous mass from such a solution. After washing with alcohol it is a white, amorphous powder. Cellulose swells up in concentrated sulphuric acid and dissolves, yielding a paste from which water precipitates a starch-like compound (amyloid), which is colored blue by iodine. After the acid has acted for some time the cellulose dissolves to form dextrine, which passes into grape sugar, when the solution is diluted with water and then boiled.

So-called parchment paper (vegetable parchment) is prepared by immersing unsized filter paper in sulphuric acid (diluted ½ with water) and then washing it with water. It is very similar to ordinary parchment, and is largely employed.

Hexacet-cellulose, $C_{12}H_{14}O_4(O.C_2H_3O)_6$, is obtained by heating cellulose (cotton) with acetic anhydride to 180°. It is an amorphous mass, soluble in concentrated acetic acid.

Cold, concentrated nitric acid, or what is better, a mixture of nitric and sulphuric acids, converts cellulose or cotton into esters or so-called *nitro-celluloses.* That these compounds are not nitro-derivatives, but true esters, is manifest, when we consider that upon treatment with alkalies they yield cellulose and nitric acid (p. 454). Alkaline sulphides and ferrous chloride also regenerate cellulose, the nitrogen escaping as ammonia or nitric oxide. The latter only is evolved by iron sulphate in a concentrated hydrochloric acid solution (*Berichte*, 13, 172).

The resulting products exhibit varying properties, depending upon their method of formation. Pure cotton dipped for a period of 3–10 minutes into a mixture of $1HNO_3$ and 2–$3H_2SO_4$, then carefully washed with water, gives gun cotton (pyroxylin). This is insoluble in alcohol and ether or even in a mixture of the two. It explodes violently if fired in an enclosed space, either by a blow or percussion. It burns energetically when ignited in the air, but does not explode. Cotton exposed for some time to the action of a warm mixture of 20 parts pulverized nitre and 30 parts concentrated sulphuric acid becomes *soluble pyroxylin,* which dissolves in ether containing a little alcohol. The solution, termed *collodion,* leaves the pyroxylin, on evaporation, in the form of a thin, transparent film, not soluble in water. It is employed in covering wounds and in photography.

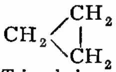
In composition gun cotton is cellulose hexa-nitrate, $C_{12}H_{14}(O.NO_2)_6O_4$, whereas the pyroxylin, soluble in ether and alcohol, is essentially a tetra nitrate, $C_{12}H_{16}(O.NO_2)_4O_6$, and a penta-nitrate, $C_{12}H_{15}(O.NO_2)_5O_5$ (*Berichte*, 13, 186).

Collodion dissolved in nitroglycerol (equal parts), yields explosive gelatine or smokeless powder.

DERIVATIVES OF CLOSED CHAINS.

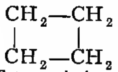
1. Polymethylene Compounds.

All the compounds considered in the preceding pages, in other words, the so-called *fatty* derivatives, contain *open*, not closed carbon chains, in which terminal and intermediate carbon atoms can be distinguished very readily (p. 42). The numerous derivatives of the benzene class, on the other hand, possess throughout a similar and hence supposed *closed* carbon chain, made up of six carbon atoms. Preceding the very stable benzene nucleus is a class of compounds discovered in recent years, in which we have closed chains. As examples we may mention **trimethylene, tetramethylene** and **pentamethylene**:—



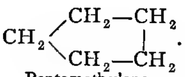
Trimethylene.

C_3H_6.



Tetramethylene.

C_4H_8.



Pentamethylene.

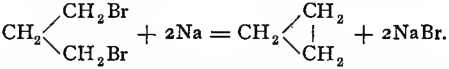
C_5H_{10}.

In these closed rings or chains of symmetrically combined C-atoms, the latter are all alike, so that isomerides are only possible by the introduction of two or several substituting groups. These parent substances and their derivatives have the same general formula, C_nX_{2n}, as the olefines and the other unsaturated compounds of the same series; the latter, however, are chiefly distinguished by their great additive power (p. 81). Indeed, the trimethylene derivatives can, by energetic action, absorb bromine and HBr (but not H_2 or I_2): the tetra- and pentamethylene compounds, on the other hand, attach themselves fully to the hexahydro-benzene derivatives.

The absence of "double linkage" in the polymethylene derivatives is very evident from the fact that they cannot be oxidized by potassium permanganate. An alkaline solution of the latter is not decolorized even upon standing for long periods (p. 82) (Baeyer, *Annalen*, 245, 146). Consult A. Baeyer, *Berichte*, 18, 2278; Sachse, *Berichte*, 23, 1363, for stereochemical views relating to the polymethylene rings.

1. TRIMETHYLENE GROUP.

Trimethylene, C_3H_6 (see above), was first obtained by heating trimethylene bromide (p. 102) with metallic sodium (*Freund*, 1882):—



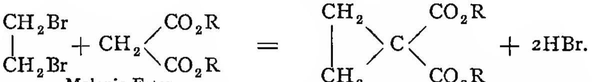
It is more easily produced by the action of alcohol and zinc dust (*Berichte*, 20, Ref. 706; 21, 1282).

It is a gas, like its isomeride, propylene. It differs from this, in that it unites with difficulty with bromine and hydriodic acid—forming trimethylene bromide and normal propyl iodide. To account for this we assume that the closed ring has been broken. Unlike the olefines it is not oxidized by potassium permanganate.

Experiments have been made to prepare *trimethylene* alcohol by acting upon α-dichlorhydrin with metallic sodium. The product, however, was allyl-alcohol.

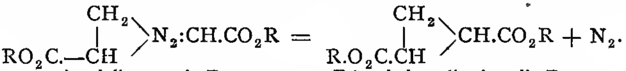
Carboxyl-derivatives of trimethylene are produced

(1) From malonic ester, acetic ester and analogous compounds by the action of alkylen bromides and sodium alcoholate (2 molecules) (Perkin, 1884) (*Annalen*, 256, 193; *Berichte*, 21, 2693):—



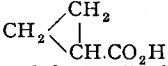
Malonic Ester. α-Trimethylene-dicarboxylic Ester.

(2) By heating the addition products of diazo-acetic esters and acrylic esters, when two nitrogen atoms split off (p. 375) (Curtius):—

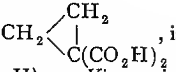


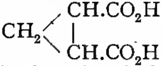
Acryl-diazo-acetic Ester. Trimethylene-dicarboxylic Ester.

Fumaric ester, $C_2H_2(CO_2R)_2$, yields trimethylene-tricarboxylic ester, and cinnamic ester yields phenyltrimethylene-tricarboxylic ester, etc., when exposed to like treatment (*Berichte*, 23, 701).

Trimethylene-carboxylic Acid, , isomeric with vinylacetic acid (isocrotonic acid, p. 238), is formed from α-dicarboxylic acid by heating it to 160°. Carbon dioxide is eliminated. It is an oil with faint odor and boils at 190°. It does not unite with bromine, like the isomeric crotonic acids (p. 238). Its *ethyl ester*, $C_4H_5O_2.C_2H_5$, from the silver salt and ethyl iodide, boils at 133°. It cannot take up bromine.

DICARBOXYLIC ACIDS.

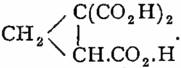
α-**Trimethylene-dicarboxylic Acid,**  $CH_2\left\langle\begin{array}{l}CH_2\\ |\\ C(CO_2H)_2\end{array}\right.$, is isomeric with hypothetical vinyl malonic acid, $C_2H_3.CH(CO_2H)_2$, or *Vinaconic Acid* (*Annalen*, 227, 25). Its diethyl ester (see above) is formed from ethylene bromide and malonic ester. Butan-tetracarboxylic ester is formed at the same time by the action of ethylene bromide upon two molecules of malonic ester. The diethyl ester is an oil that boils at 207°. The free acid melts at 140° and above 160° decomposes into CO_2 and trimethylene carboxylic acid (with butyro-lactone). Digestion with dilute sulphuric acid converts it into isomeric butyrolactone carboxylic acid (p. 468). It, however, combines with HBr, disrupting the trimethylene ring and forming bromethyl malonic acid (p. 418). It unites in an analogous manner with bromine and forms dibrom-ethyl-malonic acid, which decomposes and melts at 100–110° (*Berichte*, 18, 3414). These reactions indicate that the acid is vinyl-malonic acid. However, it cannot be further alkylized, and, unlike the mono-alkylic-malonic acids, it is not attacked by nitric acid, potassium permanganate—or even sodium amalgam (*Berichte*, 23, 704). This behavior argues in favor of its trimethylene character.

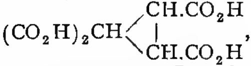
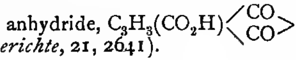
β- or (1, 2)-**Trimethylene-dicarboxylic Acid,**  $CH_2\left\langle\begin{array}{l}CH.CO_2H\\ |\\ CH.CO_2H\end{array}\right.$, is obtained (together with its anhydride) from *α*-trimethylene tricarboxylic acid, by heating the latter to 190°, when CO_2 splits off, and also from *β*-trimethylene tetracarboxylic acid by a similar loss of $2CO_2$. It crystallizes in vitreous prisms and melts at 139°. It is not affected by either potassium permanganate or sodium amalgam. Its *anhydride*, $C_3H_4(CO)_2O$, forms needles, melting at 59° and unites with water at 140°, regenerating the acid (*Berichte*, 23, Ref. 241).

γ-**Trimethylene-dicarboxylic Acid,** $C_3H_4(CO_2H)_2$. Its dimethyl ester is formed (together with the ester of glutaconic acid, p. 428) upon distilling acryl-diazo-acetic ester. It boils at 210° under a pressure of 720° mm. The free acid melts at 175°, distils unaltered, and does not form an anhydride. Potassium permanganate and sodium amalgam do not affect it.

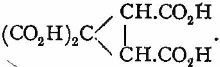
The *γ*-acid appears to have the same structural formula as the *β*-acid. It is, therefore, assumed that they are stereochemical isomerides. As the *β*-acid readily yields an anhydride, it is called the *maleïnoid*-, and the *γ*-acid *fumaroid* (1, 2)-trimethylene dicarboxylic acid (p. 424) (*Berichte*, 23, 702).

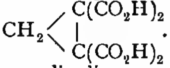
TRICARBOXYLIC ACIDS.

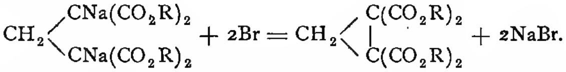
α-**Trimethylene-tricarboxylic Acid,**  $CH_2\left\langle\begin{array}{l}C(CO_2H)_2\\ |\\ CH.CO_2.H\end{array}\right.$. The trimethyl ester is obtained in a manner analogous to that employed in the case of the dicarboxylic ester. It is an agreeably smelling liquid, which boils at 276° (*Berichte*, 17, 1187). The same ester results from the union of malonic ester and *α*-bromacrylic ester. It is, therefore, probably $CH_2{:}C(CO_2H).CH(CO_2H)_2$ (*Berichte*, 20, Ref. 140, 258). The free acid crystallizes in shining needles and melts at 184°, decomposing into CO_2 and *β*-trimethylene-dicarboxylic acid.

Sym. (1, 2, 3)-**Trimethylene-tricarboxylic Acid,**  $(CO_2H)_2CH\left\langle\begin{array}{l}CH.CO_2H\\ |\\ CH.CO_2H\end{array}\right.$, is formed from *α*-tetracarboxylic acid by splitting off carbon dioxide. It melts about 150° (*Berichte*, 17, 1652). When fumaric-diazoacetic ester is heated, it yields the trimethyl ester of a trimethylene-tricarboxylic acid that is identical with the preceding. It is not changed by potassium permanganate or sodium amalgam. It melts at 220°. If it is heated to 240°, it loses water and becomes the anhydride,  $C_3H_3(CO_2H)\left<\begin{matrix}CO\\CO\end{matrix}\right>O$, melting at 187°. It boils at 265° (75 mm.) (*Berichte*, 21, 2641).

TETRACARBOXYLIC ACIDS.

α-**Trimethylene-tetracarboxylic Acid**,  $(CO_2H)_2C\left<\begin{matrix}CH.CO_2H\\|\\CH.CO_2H\end{matrix}\right.$. Its tetra-ethyl ester is obtained from malonic and dibromsuccinic esters. It boils at 246°. The free acid melts at 95–100° C., decomposing into CO_2 and symmetrical (1, 2, 3)-tricarboxylic acid.

β-**Trimethylene-tetracarboxylic Acid**,  $CH_2\left<\begin{matrix}C(CO_2H)_2\\|\\C(CO_2H)_2\end{matrix}\right.$. Its tetra-ethyl ester is produced by the action of bromine upon disodium propan-tetracarboxylic ester (p. 482):—



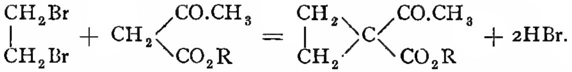
$$CH_2\left<\begin{matrix}CNa(CO_2R)_2\\CNa(CO_2R)_2\end{matrix}\right. + 2Br = CH_2\left<\begin{matrix}C(CO_2R)_2\\|\\C(CO_2R)_2\end{matrix}\right. + 2NaBr.$$

It melts at 43°, and under a pressure of 12 mm. boils at 187°.

The free acid decomposes into $2CO_2$ and *β*-trimethylene dicarboxylic acid (*Berichte*, 23, Ref. 241) when heated above 200° C.

KETONIC ACIDS.

Aceto-trimethylene Carboxylic Acid, $CH_3CO.C_3H_4.CO_2H$. Its ester is formed when ethylene bromide and sodium ethylate (2 molecules) act upon aceto-acetic ester:—



$$\begin{matrix}CH_2Br\\|\\CH_2Br\end{matrix} + CH_2\left<\begin{matrix}CO.CH_3\\CO_2R\end{matrix}\right. = \begin{matrix}CH_2\\|\\CH_2\end{matrix}\!\!>C\left<\begin{matrix}CO.CH_3\\CO_2R\end{matrix}\right. + 2HBr.$$

Diaceto-adipic ester (p. 438) results simultaneously through the action of $C_2H_4Br_2$ upon two molecules of sodium aceto-acetic ester.

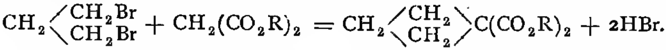
The ethyl ester is a faintly-smelling liquid, boiling about 195°. As a ketone, it combines with phenylhydrazine. HBr induces the rupture of the trimethylene ring and brom-ethyl aceto-acetic ester results (p. 340) (*Berichte*, 16, 2565). The free acid is a thick oil, which decomposes at 200° into CO_2 and **aceto-trimethylene**, $CH_3.CO_3.C_3H_5$, which boils at 113° (*Berichte*, 22, Ref. 502, 572; 22, 1210).

Benzoyl-trimethylene Carboxylic Acid, $C_6H_5.CO\ C_3H_4.CO_2H$, is produced, like the preceding, from benzoyl-acetic ester. It forms large prisms, melts at 149°, and decomposes into CO_2 and **benzoyl-trimethylene**, $C_6H_5.CO.C_3H_5$. An oil, boiling at 239°. It forms an oxime with hydroxylamine (*Berichte*, 19, 2565).

Boiling alkalies do not decompose benzoyl- and aceto-trimethylene carboxylic acids. Herein they differ from allyl aceto-acetic and allyl-benzoyl acetic acids. In a similar manner paranitro-benzoyl acetic ester yields paranitrobenzoyl trimethylene tricarboxylic ester (*Berichte*, 18, 958).

2. TETRAMETHYLENE DERIVATIVES.

Tetramethylene derivatives (p. 515) are obtained by acting upon malonic ester with trimethylene bromide and sodium alcoholate (2 molecules) (Perkin):—

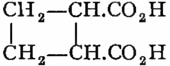


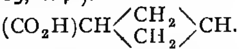
$$CH_2\left\langle\begin{array}{l}CH_2Br\\CH_2Br\end{array}\right. + CH_2(CO_2R)_2 = CH_2\left\langle\begin{array}{c}CH_2\\CH_2\end{array}\right\rangle C(CO_2R)_2 + 2HBr.$$

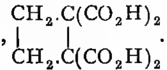
Tetramethylene-carboxylic Acid, $C_4H_7.CO_2H$, isomeric with allyl-acetic acid, is formed from the dicarboxylic acid by withdrawal of CO_2. It is an oil, which boils at 194°, and has an odor like that of a fatty acid.

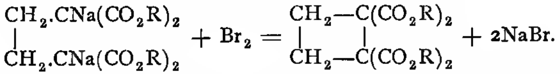
Not tetramethylene, C_4H_8, but **Ditetramethylene Ketone,** $C_4H_7.CO.C_4H_7$, is formed by distilling its lime salt. This is a liquid, with an odor like that of peppermint. It boils at 205° (*Berichte*, 19, 3113).

α-Tetramethylene-dicarboxylic Acid, $C_4H_6(CO_2H)_2$. Its diethyl ester (isomeric with allyl malonic ester, p. 430) is formed (together with pentan-tetracarboxylic ester, p. 482) from trimethylene bromide and malonic ester (*Berichte*, 21, 2693). It is an oil with camphor-like odor, and boils at 224° (*Berichte*, 16, 1787). The free acid dissolves easily in ether and benzene, but not in chloroform and benzine; it crystallizes in shining prisms, and melts at 155°, decomposing into the monocarboxylic acid and CO_2.

β-Tetramethylene Dicarboxylic Acid,  $\begin{array}{l}CH_2—CH.CO_2H\\|\qquad\quad|\\CH_2—CH.CO_2H\end{array}$, results upon heating tetracarboxylic acid (see below) to 180° C. with water. It splits off $2CO_2$ groups. It is crystalline and melts at 130° C. At 300° it loses water and becomes the anhydride $C_4H_6(CO)_2O$, melting at 77° (*Berichte*, 19, 2042).

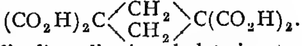
The third **Tetramethylene Dicarboxylic Acid,**  $(CO_2H)CH\left\langle\begin{array}{c}CH_2\\CH_2\end{array}\right\rangle CH.CO_2H$, appears to be **tetrylene dicarboxylic acid,** whose ester results from the action of α-chlorpropionic ester and sodium ethylate. It boils above 230° (*Annalen*, 208, 333). Its free acid is crystalline, melts at 171° and sublimes in needles. The acid and the ester do not combine with nascent hydrogen, HBr or bromine. Consult *Berichte*, 23, Ref. 432 for its anhydride derivatives.

α-Tetramethylene Tetracarboxylic Acid,  $\begin{array}{l}CH_2.C(CO_2H)_2\\|\qquad|\\CH_2.C(CO_2H)_2\end{array}$. Its ethyl ester is produced by the action of bromine (as with β trimethylene tetracarboxylic ester) upon butan-tetracarboxylic ester (its disodium compound):—



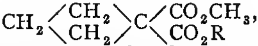
$$\begin{array}{l}CH_2.CNa(CO_2R)_2\\|\\CH_2.CNa(CO_2R)_2\end{array} + Br_2 = \begin{array}{l}CH_2—C(CO_2R)_2\\|\qquad|\\CH_2—C(CO_2R)_2\end{array} + 2NaBr.$$

The free acid is crystalline, melts at 145–150° C., and decomposes into $2CO_2$ and β tetramethylene dicarboxylic acid (*Berichte*, 19, 2041).

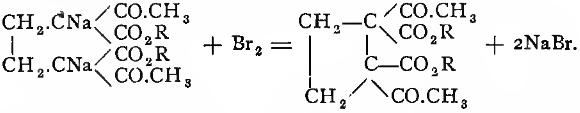
β-Tetramethylene Tetracarboxylic Acid,  $(CO_2H)_2C\left\langle\begin{array}{c}CH_2\\CH_2\end{array}\right\rangle C(CO_2H)_2$. Its tetraethyl ester has been obtained from the disodium dicarboxyl-glutaric ester by means of methylene iodide (*Berichte*, 23, Ref. 240).

KETONIC ACIDS.

When trimethylene bromide acts upon acetoacetic ester the product is not the analogous—

Aceto-tetra-methylene Carboxylic Ester,  $CH_2\left\langle\begin{matrix}CH_2\\CH_2\end{matrix}\right\rangle C\left\langle\begin{matrix}CO_2CH_3\\CO_2R\end{matrix}\right.$, but the ester of an *isomeric* acid, which probably represents the carboxylic acid of the anhydride of acetobutyl alcohol, as it breaks up, when distilled, into CO_2 and that anhydride (p. 322). $C_3H_6Br_2$ also acts analogously upon benzoyl-aceto-acetic ester and acetone dicarboxylic ester (*Berichte*, 19, 2557; 21, 736).

Diaceto-tetramethylene Dicarboxylic Acid, $(CH_3CO)_2C_4H_4(CO_2H)_2$, is a true diketonic acid. Its diethyl ester is produced in the action of bromine upon the disodium compound of diaceto-adipic ester (see above):—



$$\begin{matrix}CH_2.CNa\left\langle\begin{matrix}CO.CH_3\\CO_2R\end{matrix}\right.\\ | \\ CH_2.CNa\left\langle\begin{matrix}CO_2R\\CO.CH_3\end{matrix}\right.\end{matrix} + Br_2 = \begin{matrix}CH_2-C\left\langle\begin{matrix}CO.CH_3\\CO_2R\end{matrix}\right.\\ | \qquad | \\ | \qquad C-CO_2R \\ CH_2 \diagup \diagdown CO.CH_3\end{matrix} + 2NaBr.$$

It is a liquid, which is colored a violet red by ferric chloride. The free acid from it crystallizes with $2H_2O$, which it loses at 80°. When anhydrous the acid melts, with decomposition, at 210° (*Berichte*, 19, 2048).

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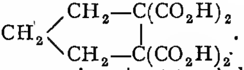
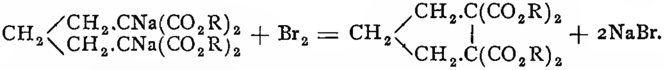
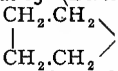
3. PENTAMETHYLENE DERIVATIVES.

Pentamethylene-tetra-carboxylic Acid,  $CH_2\left\langle\begin{matrix}CH_2-C(CO_2H)_2\\ | \\ CH_2-C(CO_2H)_2\end{matrix}\right.$. Bromine converts disodium pentan-tetra-carboxylic ester into its tetraethyl ester (*Berichte*, 18, 3246):—



$$CH_2\left\langle\begin{matrix}CH_2.CNa(CO_2R)_2\\CH_2.CNa(CO_2R)_2\end{matrix}\right. + Br_2 = CH_2\left\langle\begin{matrix}CH_2.C(CO_2R)_2\\ | \\ CH_2.C(CO_2R)_2\end{matrix}\right. + 2NaBr.$$

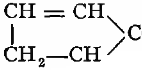
The free acid, from the oily ester, decomposes when heated to 200–220° into $2CO_2$ and **Pentamethylene-dicarboxylic Acid,** $C_5H_8(CO_2H)_2$, crystallizing in warty masses, melting at 160°. At 300° it yields water and the anhydride, $C_5H_8(CO)_2O$, melting about 65° (*Berichte*, 18, 3251).

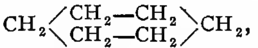
Ketopentamethylene,  $\left.\begin{matrix}CH_2.CH_2\\ | \\ CH_2.CH_2\end{matrix}\right\rangle CO$, may be obtained by distilling calcium adipate. If two of its O-atoms be replaced by two chlorine atoms, and further acted upon with nascent hydrogen the product will be **Pentamethylene,** C_5H_{10}. This is a liquid boiling at 30–31° (J. Wislicenus).

Derivatives of (1, 2)- and (1, 3)-diketo pentamethylene have been prepared by oxidizing orthoamidophenol and pyrocatechol with chlorine. The 'six-membered' benzene ring is changed to the 'five-membered' pentamethylene ring (Zincke, *Berichte*, 21, 2718; 23, 813, 2200). The naphthalene ring by similar treatment yields the indene ring.

Diketo-pentamethylene derivatives have been prepared by the action of chlorine upon alkaline solutions of phenol and chloranilic acid (Hantzsch, *Berichte* 22, 1238 and 2841). Consult *Berichte*, 22, 2827; 23, 1478 for the transformations of pentamethylene compounds into derivatives of benzene, pyridine and thiophene (*Berichte* 22, 2827; 23, 1478).

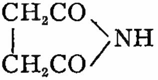
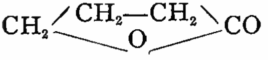
Leuconic Acid, $C_5O_5 + 5H_2O$, and **Croconic Acid**, $C_5O_5H_2$, keto-derivatives of pentamethylene, will be discussed together with the triquinoline derivatives.

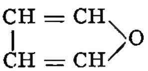
Methronic acid, carbopyrotritartaric acid and their compounds are considered derivatives of hypothetical **ketopentene**,  $\begin{matrix} CH = CH \\ | \\ CH_2—CH \end{matrix} \rangle CO$, **tetrylone.**

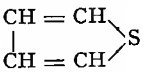
Hexamethylene, C_6H_{12} =  $CH_2 \langle \begin{matrix} CH_2—CH_2 \\ CH_2—CH_2 \end{matrix} \rangle CH_2$, is described under the benzene derivatives as hexahydrobenzene (benzene hydride).

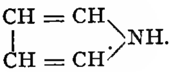
A **Heptamethylene** derivative, C_7H_{14}, seems to have been obtained from diaceto-adipic ester (*Berichte*, 19, 2052).

FURFURANE, THIOPHENE AND PYRROL DERIVATIVES.

The polymethylene closed chains consist of carbon atoms only; but there are those which in addition to the C-atoms also contain atoms of other polyvalent elements (oxygen, sulphur and nitrogen). Closed chains of this class are numerous among the fatty bodies, *e. g.*, the anhydrides of the dicarboxylic acids (succinic anhydride, p. 412) succinimide,  $\begin{matrix} CH_2CO \\ | \\ CH_2CO \end{matrix} \rangle NH$ (p. 412), parabanic acid, the derivatives of cyanuric acid and melamine (p. 290), etc., etc. In all of them 2CO are usually united by O, S or N, and the compounds are very unstable and change rapidly to the normal open chains. The chain of the γ-lactone contains but one CO-group,  $CH_2 \langle \begin{matrix} CH_2—CH_2 \\ O \end{matrix} \rangle CO$ (p. 351), and is more stable. **Furfurane**, C_4H_4O, **Thiophene**, C_4H_4S, and **Pyrrol**, $C_4H_4(NH)$, consist of closed chains in which the linking is even firmer than in the derivatives mentioned. These bodies attach themselves to the benzene series; their constitution is very probably represented by the following structural formulas:—

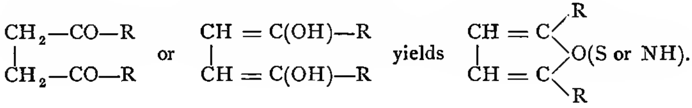

Furfurane.


Thiophene.

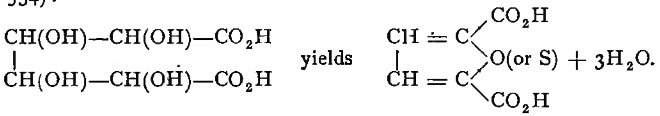

Pyrrol.

In accordance with these formulas the three parent substances and their derivatives exhibit many striking analogies in their entire deportment. Thus furfurane, thiophene and pyrrol yield bluish violet dyestuffs with isatin and sulphuric acid, and compounds having a violet red color, when acted upon with phenanthraquinone and sulphuric acid. Again, these compounds, and all those obtained from them, exhibit a striking and astonishing similarity to benzene. This is especially true of thiophene. All the peculiar reactions of benzene derivatives; those which distinguish the latter from the fat-bodies, are shown by furfurane, pyrrol and thiophene. Thus, the halogens produce substitution derivatives and not additive compounds (as with the olefines). This would scarcely be expected from the fact that double unions occur in furfurane, etc., etc.

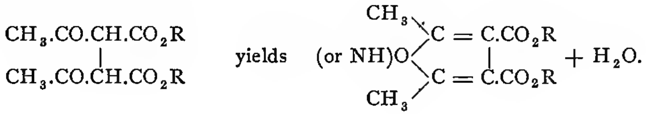
The synthetic methods, applied in the formation of furfurane, pyrrol and thiophene, correspond in every particular to the accepted structural formulas. All three compounds are obtained from γ-diketone derivatives, in which the atomic group—$CO.CH_2.CH_2CO$—is present, by the separation of water and the linking of the two carbonyl carbon atoms by O, S or N (p. 329). It may be assumed that here the diketone form sustains a transposition into the unstable, unsaturated dihydroxyl form (syntheses of Paal, *Berichte*, 17, 2757; 18, 367), etc.:—



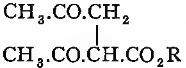
Analogous hydroxyl derivatives react in harmony with this view; thus, by withdrawing water from mucic and isosaccharic acids furfurane dicarboxylic acid is formed, and by distillation with BaS thiophene carboxylic acid is the product (p. 534):—



Diaceto-succinic acid (p. 437) yields dimethyl furfurane dicarboxylic acid and dimethylpyrrol dicarboxylic acid (syntheses of Knorr, *Berichte*, 17, 2863; 18, 299, etc.):—



In a similar manner acetonyl-acetoacetic ester,

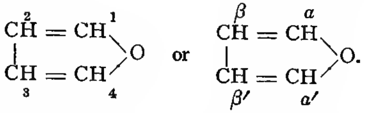


$$\begin{array}{l} CH_3.CO.CH_2 \\ \quad | \\ CH_3.CO.CH.CO_2R \end{array}$$

(p. 340), yields the dimethyl monocarboxylic acids, etc. Consult *Berichte*, 21, 2932, 3451 for other furfurane derivatives.

To distinguish the possible isomerides the replaceable hydrogen atoms, or the

C-atoms in furfurane, thiophene and pyrrol are designated by numbers as with benzene:—



The positions 1 and 4 are equal in value, also 2 and 3. The first are also termed α-, the latter β-positions. It is obvious that the mono-derivatives of furfurane, etc., can exist in two isomeric forms (α-derivatives and β-derivatives).

1. THE FURFURANE GROUP.*

Furfurane, C_4H_4O (see above), was formerly held to be tetrolphenol, $C_4H_3.OH$. It was first obtained by distilling barium pyromucate (p. 526) with soda-lime: ($C_4H_3O.CO_2H = C_4H_4O + CO_2$). It is present in the distillation products of pine wood. It is a liquid, insoluble in water, has a peculiar odor, and boils at 32°. Metallic sodium has no effect upon it, nor does it combine with phenyldrazine. It yields dye substances with isatin and phenanthraquinone (see above). It reacts very violently with hydrochloric acid, and forms a brown amorphous substance (like pyrrol red, p. 539). A pine shaving moistened with hydrochloric acid, assumes a green color when brought in contact with the vapors of furfurane.

Brominated derivatives can be obtained from brom-pyromucic acids, or by the direct action of bromine upon furfurane. Other addition products result from an excess of bromine.

ALKYLIZED FURFURANES.

Methyl Furfurane, $C_4H_3(CH_3)O$, is in all probability *sylvan*, which occurs in pine tar oil. It boils at 63° (*Berichte*, 13, 881).

α-Dimethyl Furfurane, $C_4H_2(CH_3)_2O(1, 4)$, is formed by the distillation of carbopyrotritartaric acid (p. 528), and has been directly synthesized from acetonyl acetone upon heating it with $ZnCl_2$ or P_2O_5 (p. 328). A mobile liquid with a peculiar odor. It boils at 94°. It is resinified when heated with concentrated mineral acids (*Berichte*, 20, 1085).

It regenerates acetonyl acetone when it is heated with dilute hydrochloric acid to 170°.

α-Methyl-phenyl Furfurane, $C_4H_2\left\{\begin{matrix}CH_3\\C_6H_5\end{matrix}\right\}O(1,4)$, is produced from acetophenone-acetone, $\begin{matrix}CH_3.CO.CH_3\\|\\CH_3.CO.C_6H_5\end{matrix}$, upon digesting it with acetic anhydride, or hydrochloric acid, (*Berichte*, 17, 915 and 2759). It crystallizes from alcohol in shining needles, melting at 42°. The compound boils at 235–240° C. Sodium, in alcoholic solution, converts it into the tetrahydro-compound, $C_{11}H_{14}O$.

Nitroethylene Furfurane, $C_4H_3O.CH:CH(NO_2)$. This results from the condensation of furfurol, $C_4H_3O.CHO$, with nitroethane. It consists of yellow

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* Compare "Das Furfuran, etc," von A. Bender, 1889.

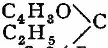
needles, melting at 75° (*Berichte*, 18, 1362). By nitration it passes into nitrofurfurane-nitroethylene.

Butylene Furfurane, $C_4H_3O.C_4H_7$, has been obtained by the condensation of furfurol with isobutyric acid (see below). A liquid, boiling at 153° (*Berichte*, 17, 850).

Diphenyl Furfurane, $C_4H_2(C_6H_5)_2O$, see *Berichte*, 21, 3057. **Triphenyl Furfurane**, $C_4H(C_6H_5)_3O$, see *Berichte*, 21, 2933. **Tetraphenyl Furfurane**, $C_4(C_6H_5)_4O$, Lepidene, *Berichte*, 22, 2880.

ALCOHOLS.

Furfuryl Alcohol, $C_5H_6O_2 = C_4H_3O.CH_2OH$ (the monovalent group C_4H_3O is called furfur-), results from the action of sodium amalgam and acetic acid upon the aldehyde furfurol, but more easily by treatment with aqueous caustic potash (*Berichte*, 19, 2154). Furfurane carboxylic acid is produced at the same time ($2C_4H_3O.CHO + H_2O = C_4H_3O.CH_2OH + C_4H_3O.CO_2H$). Ether extracts it as a colorless syrup, which in drying becomes gummy. It is colored green by hydrochloric acid.

Ethylfurfur-Carbinol,  $\begin{matrix}C_4H_3O\\C_2H_5\end{matrix}\!>\!CH.OH$, results from the action of furfurol and zinc ethide. It boils at 180° (*Berichte*, 17, 1968).

ALDEHYDES AND KETONES.

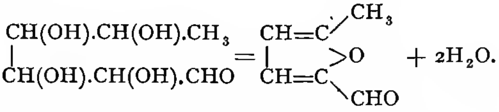
α-Furfurol, $C_5H_4O_2 = C_4H_3O.CHO$, (1–4), the aldehyde of furfuryl alcohol, or of pyromucic acid, is produced in the distillation of bran with dilute sulphuric acid, or of sugar, as well as most carbohydrates and glucosides. When present in even the merest traces it can be detected by the red coloration given by aniline or xylidine (*Berichte*, 20, 541). It yields a violet coloration with α-naphthol and sulphuric acid (*Berichte*, 21, 2744).

Preparation.—Distil 1 part of bran with 1 part sulphuric acid; dilute with 3 parts of water. Throw out the furfurol from the distillate by the addition of common salt, and repeat the distillation (*Annalen*, 116, 257; 156, 198). The product obtained on distilling algæ with sulphuric acid consists chiefly of furfurol and methyl furfurol (*Berichte*, 23, Ref. 154).

Furfurol is a colorless liquid with an aromatic odor. Its specific gravity at 13° is 1.163. It boils at 162°. It is soluble in 12 parts of water at 13°, and very soluble in alcohol. It becomes brown on exposure to the air, and shows all the properties of an aldehyde. It combines with bisulphites, passes into furfuryl alcohol under the influence of sodium amalgam, and is changed to pyromucic acid by argentic oxide, and to the alcohol and acid through the action of caustic potash (this is similar to the behavior of the benzaldehydes). It yields **furfuraldoxime**, $C_4H_3O.CH:N(OH)$ with hydroxylamine; it melts at 89° and boils at 205° (*Berichte*, 23, 2336). It unites similarly with phenylhydrazine, forming a *hydrazone*, $C_4H_3O.CH:(N_2H)C_6H_5$, melting at 96°. Furthermore, furfurol manifests all the condensation reactions of benzaldehyde (see below). It combines with dimethylaniline to form a green dye-stuff, corresponding to malachite green.

In furfurol the aldehyde group occupies the α-position. This is evident from the fact that the furonic acid, obtained from it, can be reduced to normal α-pimelic acid (p. 528).

α-**Methyl Furfurol**, $C_4H_2(CH_3)O.CHO$, occurs together with furfurol in wood oil. It can be isolated from this by fractional crystallization (*Berichte*, 22, 608). It is also present in the product obtained by distilling varec with sulphuric acid (*Berichte*, 22, Ref. 751). When rhamnose is distilled with sulphuric acid, it results, and may, therefore, be considered as the anhydride of rhamnose (*Berichte*, 22, Ref. 752):—



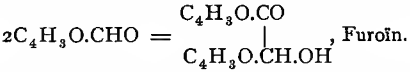
It is an oil, boiling at 184–186°. It may be oxidized to methyl pyromucic acid. Alcohol and sulphuric acid color it green.

Furfurol condenses with fatty aldehydes and ketones, forming furfuryl-aldehydes and ketones having unsaturated side-chains. As in the case of benzaldehyde this reaction here proceeds with ease on digesting with sodium hydroxide (*Berichte*, 12, 2342). Thus acetaldehyde or paraldehyde reacts according to the equation:—

$$C_4H_3O.CHO + CH_3.CHO = C_4H_3O.CH{:}CH.CHO, \text{ Furfur-acroleïn.}$$

Furfur-acroleïn, $C_7H_6O_2$, melts at 51° and boils above 200°. Propionic aldehyde yields **Furfur-crotonaldehyde**, $C_4H_3O.CH{:}C(CH_3)CHO$, which is an oil with ethereal odor. With acetone, furfurol forms **Furfur-acetone**, $C_4H_3O.CH{:}CH.CO.CH_3$, etc.

When furfurane is exposed to the action of KCN in alcoholic solution, it suffers a peculiar transposition into **Furoïn** (like that of benzaldehyde to benzoïn):—



$$2C_4H_3O.CHO = \begin{array}{c} C_4H_3O.CO \\ | \\ C_4H_3O.CH.OH \end{array}, \text{ Furoïn.}$$

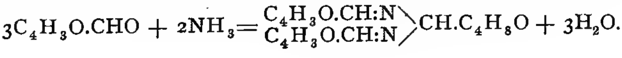
Furoïn, $C_{10}H_8O_4$, is crystalline and melts at 135°. The oxygen of the air oxidizes it, when in alkaline solution, to **Furil**, $C_{10}H_6O_4 = C_4H_3O.CO.CO.C_4H_3O$, a compound analogous to benzil. KCN decomposes furil into furfurol and the ester of pyromucic ester (*Berichte*, 16, 658). When furil is digested with caustic potash it becomes **furilic acid** (analogous to benzilic acid (see this).

Mixed furoïns, *e.g.*, **Benzfuroïn**, $C_4H_3.CO.CH(OH).C_6H_5$, are produced, like furoïn from furfurol, by letting KCN act upon a mixture of furfurol and benzaldehyde.

AMIDE DERIVATIVES.

Furfurylamine, $C_4H_3O.CH_2.NH_2$, is obtained by reducing furfuro-nitrile, $C_4H_3O.CN$ (p. 526), and furfurol hydrazone (p. 524) with sodium amalgam. It is a liquid, boiling at 146° (*Berichte*, 20, 399).

Furfuramide, $(C_5H_4O)_3N_2$, results from the action of aqueous ammonia upon furfurol (same as hydrobenzamide from benzaldehyde, see this):—



$$3C_4H_3O.CHO + 2NH_3 = \begin{array}{l} C_4H_3O.CH{:}N \\ C_4H_3O.CH{:}N \end{array}\!\!\Big\rangle CH.C_4H_3O + 3H_2O.$$

It is very soluble in alcohol and ether. It crystallizes in yellowish-colored needles, melting at 117°. It has a neutral reaction, and does not combine with acids. Acids and boiling water decompose it into furfurol and ammonia. If heated to 120°, or if boiled with KOH, it undergoes a transposition (like that of hydrobenzamide into amarine) into the isomeric base, Furfurin, $C_{15}H_{12}N_2O_3$, melting at 116°, and forming salts with one equivalent of the acids. It is perfectly analogous to amarine of the benzene series.

Benzene amido-compounds of varying composition are produced by the union of furfurol with anilines and aromatic diamines (1 and 2 molecules of the same) (*Annalen*, 201, 355). In this way, dye-stuffs, resembling rosaniline, have been produced. Their salts show an intensely red color, *e.g.*, furoxylidine, $C_4H_3O.CH(C_8H_8.NH_2)_2$, and answer for the detection of furfurol (*Berichte*, 20, 541).

ACIDS.

α-**Furfurane-carboxylic Acid,** $C_5H_4O_3 = C_4H_3O.CO_2H$, *pyromucic acid*, is obtained by the oxidation of furfurol with silver oxide or caustic potash, and in the distillation of mucic and isosaccharic acids (p. 522); it, therefore, contains the carboxyl group in the *α*-position.

To prepare pyromucic acid, distil about 30 grams of mucic acid from a retort (*Annalen*, 165, 256). A better course is to let alcoholic caustic potash act upon furfurol (*Annalen*, 165, 279).

Pyromucic acid is very soluble in hot water and alcohol. It crystallizes in needles or leaflets, melting at 134°, and subliming at 100° C.

Its *ethyl ester*, $C_4H_3O.CO_2.C_2H_5$, melts at 34° and boils at 210° C. Its *chloride*, $C_4H_3O.COCl$, obtained by distilling the acid with PCl_5, boils at 170°. Ammonia converts this into an *amide*, $C_4H_3O.CO.NH_2$, which is changed into *furfuryl-nitrile*, $C_4H_3O.CN$, by PCl_3.

Bromine vapor converts pyromucic acid into a *tetrabromide*, $C_4H_3OBr_4.CO_2H$, which is oxidized to dibromsuccinic acid by chromic acid. Fumaric acid results on evaporating pyromucic acid with bromine water (2 molecules). An excess of bromine or chlorine water produces mucobromic acid, $C_4H_2Br_2O_3$, and mucochloric acid, $C_4H_2Cl_2O_3$ (p. 427).

α-**Brom-pyromucic Acid,** $C_4H_2BrO.CO_2H$ (4 or *α'*) is formed by heating the tetrabromide, and by brominating pyromucic acid in glacial acetic acid solution. It consists of pearly leaflets, melting at 184° (*Berichte*, 19, Ref. 241). *β*-**Brom-pyromucic Acid,** $C_4H_2BrO.CO_2H$, from the two dibrompyromucic acids and zinc, melts at 129°.

Two **Dibrompyromucic Acids,** $C_4HBr_2.CO_2H$, have been obtained from pyromucic tetrabromide by means of alcoholic soda. The *ββ'*-acid melts at 192°, the *βα'*-acid at 168° (*Berichte*, 17, 1759).

Nitropyromucic Acid, $C_4H_2(NO_2)O.CO_2H$, is formed by nitrating furfurane dicarboxylic acid with a mixture of nitric and sulphuric acids, and by oxidizing nitroethylene-nitrofurfurane (p. 523). It crystallizes from water in bright yellow plates, melting at 183° (*Berichte*, 18, 1362).

Isopyromucic Acid, $C_5H_4O_3$, apparently does not exist (*Berichte*, 23, Ref. 154).

Methyl Pyromucic Acid, $C_5H_3(CH_3)O_3$, has been obtained by the oxidation of methyl furfurol. It melts at 109° (*Berichte*, 22, 608). Bromine water converts it into aceto-acrylic acid (*Berichte*, 23, 452).

Methyl Furfurane Acetic Acid, $C_4H_2O\begin{matrix}\diagup CH_3 \\ \diagdown CH_2.CO_2H,\end{matrix}$ Sylvan-acetic acid, has been obtained by the condensation of glyoxal with aceto-acetic ester, etc. It melts at 137° (*Berichte*, 21, Ref. 636).

αα-**Dimethyl Furfurane-*β*-carboxylic Acid, Pyrotritartaric Acid,** $C_7H_8O_3 = C_4H(CH_3)_2O.CO_2H$ (*Berichte*, 20, 1074), **Uvinic Acid,** was first obtained from tartaric acid (with pyroracemic) by distillation. It can also be produced from pyroracemic acid by protracted boiling with baryta water or sodium acetate, etc. It has been synthetically prepared (its ethyl ester) by the action of fuming hydrochloric acid upon acetonyl aceto-acetic ester (*Berichte*, 17, 2765). It also results from carbopyrotritartaric acid and from methronic acid (p. 528) by the splitting-off of carbon dioxide. This occurs when the acid is heated beyond its melting point. This is the best method for the obtainment of uvinic acid.

Pyrotritartaric acid dissolves with difficulty even in hot water (in 400 parts), from which it crystallizes in needles, melting at 135° C. It sublimes readily and is quite volatile with steam. When heated to 150-160° with steam it breaks up into carbon dioxide and acetonyl acetone (p. 328). Rapidly distilled, it decomposes into carbon dioxide and *α*-dimethyl furfurane. See *Berichte*, 20, 1077, for brompyrotritartaric acid.

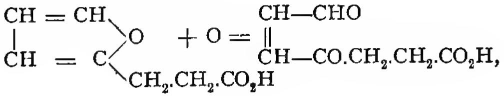
αα-**Methylphenylfurfurane-carboxylic Acid,** $C_4H\begin{pmatrix}CH_3 \\ C_6H_5\end{pmatrix}O.CO_2H$. Its ethyl ester is produced by the action of hydrochloric acid upon acetophenon-aceto-acetic ester, $\begin{matrix}C_6H_5.CO.CH_2 \\ | \\ CH_3.CO.CH.CO_2R\end{matrix}$ (p. 522). The free acid, obtained by saponification, melts at 181°, and upon boiling with dilute sulphuric acid yields methylphenylfurfurane (p. 524) (*Berichte*, 17, 2764).

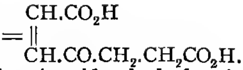
Furfurane **acids,** with unsaturated side chains, are produced in the condensation of furfurol and fatty acids, on heating it with the anhydrides and sodium salts of the fatty acids. This is analogous to the formation of cinnamic acid (see this) from benzaldehyde. Furfur-acrylic acid results on heating furfurane with acetic anhydride and sodium acetate:—

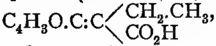
$$\underset{\text{Furfurane.}}{C_4H_3O.CHO} + CH_3.CO_2Na = \underset{\text{Furfur-acrylic Acid.}}{C_4H_3O.CH{:}CH.CO_2Na} + H_2O.$$

Furfur-acrylic Acid, $C_7H_6O_3$. This acid is also formed on oxidizing furfur-acroleïn with silver oxide; furfur-malonic acid also yields it (*Berichte*, 21, 1081). It dissolves with difficulty in water, crystallizes in long needles, has an odor like that of cinnamon, and melts at 135°. When it is heated with hydrochloric acid it becomes acetone-diacetic acid. Sodium amalgam converts it into

Furfur-propionic Acid, $C_4H_3O.CH_2.CH_2.CO_2H$, melting at 51°. Bromine disrupts the furfurane ring in this compound, and the product is the aldehyde of furonic acid (*Berichte*, 10, 695):—



which silver oxide converts into **furonic acid**, $C_7H_8O_5$ =  $\begin{matrix} CH.CO_2H \\ \| \\ CH.CO.CH_2.CH_2CO_2H. \end{matrix}$ Needles, melting at 180°. Sodium amalgam changes furonic acid to hydrofuronic acid, $C_7H_{10}O_5$, which passes into normal pimelic acid, $C_5H_{10}(CO_2H)_2$ (p. 421), on heating it with hydriodic acid and phosphorus (*Berichte*, 11, 1358).

Furfur-angelic Acid, $C_9H_{10}O_3$ =  $C_4H_3O.C:C\begin{matrix} \diagup CH_2.CH_3, \\ \diagdown CO_2H \end{matrix}$ from furfurol and butyric acid (see above), melts at 88°, and passes into the corresponding **Furfur-valeric Acid** under the influence of sodium amalgam.

DICARBOXYLIC ACIDS.

a-**Furfurane Dicarboxylic Acid**, $C_6H_4O_5 = C_4H_2O(CO_2H)_2$, *dehydromucic acid*, is produced by heating mucic acid to 100° with hydrochloric and hydrobromic acid (p. 522). It dissolves with difficulty in water, crystallizes in needles, and when heated does not melt but breaks up into carbon dioxide and pyromucic acid.

a-**Dimethylfurfurane-*β*-dicarboxylic Acid**, $C_8H_8O_5 = C_4(CH_3)_2O(CO_2H)_2$, **carbopyrotritartaric acid**, results upon boiling diacetsuccinic ester (p. 437) with dilute sulphuric acid. When the ester is heated alone, or is acted upon by concentrated hydrochloric acid, the primary ester, $C_8H_7O_5.C_2H_5$, is produced, but if allowed to stand with sulphuric acid, the diethyl ester, $C_8H_6O_5(C_2H_5)_2$ (*Berichte*, 17, 2864), is the product. Carbopyrotritartaric acid crystallizes from hot water in minute needles, melting at 231°, and at higher temperatures breaks up into carbon dioxide and pyrotritartaric acid.

Methronic Acid, $C_8H_8O_5 = C_4(CH_3)_2O(CO_2H)_2$, is isomeric with carbopyrotritartaric acid. It is produced by digesting aceto-acetic ester with sodium succinate and acetic anhydride (Fittig, *Berichte*, 18, 3410). By similar action, aceto-acetic ester and pyrotartaric acid yield methyl methronic acid, and benzoyl-acetic ester and succinic acid form phenylmethronic acid (*Berichte*, 21, 2134). Methronic acid is more soluble in water and melts at 204°. At higher temperatures it also decomposes into carbon dioxide and pyrotritartaric acid. It is, therefore, very probable that methronic acid and carbopyrotritartaric acid, with their compounds, are derived from furfurane (Knorr). R. Fittig thinks that they are derivatives of hypothetical *tetrylone* (p. 521) (*Berichte*, 22, 146).

Isocarbopyrotritartaric Acid, $C_8H_8O_5$, of unknown constitution, is isomeric with methronic and carbopyrotritartaric acids. It is formed when diaceto-succinic ester is distilled (*Berichte*, 22, 158).

THIOPHENE GROUP.*

Thiophene, C_4H_4S, an analogue of furfurane, C_4H_4O (p. 521), exhibits, in a more marked degree than the latter, a complete analogy with benzene, C_6H_6; its derivatives are perfectly analogous to those of benzene. It may be viewed as a benzene, in which one of the three acetylene groups, CH:CH, has been replaced by S;

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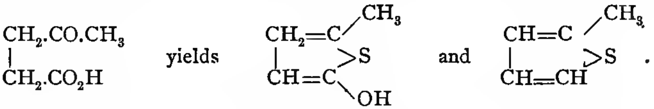
* V. Meyer, *Die Thiophengruppe*, 1888.

the original properties not being essentially altered. By the replacement of the 4-H atoms in thiophene, by other elements or groups, we obtain innumerable derivatives, in all respects analogous to those derived from benzene. All thiophene compounds give an intense blue coloration—the indophenin reaction, *Berichte*, 16, 1473—when mixed with a little isatin and concentrated sulphuric acid. The methods of forming the thiophenes synthetically from (1, 4)- or γ-dicarboxyl compounds, have been given on pp. 329, 522). It may be well to again direct attention to the ready transposition of the γ-ketonic acids, which yield oxythiophenes when heated with P_2S_5, or thiophene hydrocarbons if P_2S_3 be employed (*Berichte*, 19, 551; 23, 1495):—



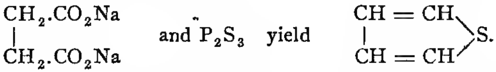
Lævulinic Acid. (1, 4)-Oxythiotolene. α-Thiotolene.

(1, 3)-Thioxene, $C_4H_2S(CH_3)_2$ (*Berichte*, 20, 2017), and (1, 2)-thioxene (*Berichte*, 20, 2577) are similarly produced from α-methyl-lævulinic acid, $CH_3.CO.CH_2.CH(CH_3).CO_2H$, and β-methyl-lævulinic acid, $CH_3.CO.CH.CH_3.CH_2.CO_2H$ (*Berichte*, 21, 3451). The isomerisms of thiophene derivatives correspond to those of furfurane and are similarly named (p. 523). The α-derivatives (those in which the H-atom is adjacent to the sulphur-atom) were formerly termed β-derivatives, and the real β-derivatives considered as and designated γ-derivatives. In the following pages the correct designations, corresponding to the thiophene formula (p. 521), have been introduced (*Berichte*, 19, 2890).

The thiophene bodies were discovered by V. Meyer, in 1883.

Thiophene, C_4H_4S, and its homologues, occur in ordinary, impure coal tar. The individual thiophenes are contained in the corresponding commercial benzene hydrocarbons (about 6%). They have the same boiling points as the latter. Thiophene is present in benzene, methyl thiophene (thiotolene), $C_4H_3S.CH_3$, in toluene, $C_6H_5.CH_3$, dimethyl thiophene (thioxene), $C_4H_2S(CH_3)_2$, in xylene, $C_6H_4(CH_3)_2$, etc. Benzenes containing thiophene show the indophenin reaction (see above). The latter is not observed until the benzenes have been fully purified by shaking them with sulphuric acid. The latter withdraws the thiophenes.

Thiophene is synthesized by various reactions: By conducting ethyl sulphide through tubes heated to redness or passing ethylene or illuminating gas over heated pyrite, FeS_2; and by heating crotonic acid, butyric acid, etc., with P_2S_5. It is produced quite abundantly upon heating a mixture of succinic anhydride, or sodium succinate with P_2S_3 (Volhard):—



Preparation.—Shake ordinary benzene for some hours with sulphuric acid (10–4 per cent.), then separate the black acid-layer (containing the thiophene as a sulpho-acid) from the benzene, and dilute the former immediately with water. Some benzene sulphonate is usually present with the thiophene sulphonate, but its quantity diminishes as the quantity of sulphuric acid is decreased. When but 4 per cent. of the latter is present the thiophene-sulphonate is almost pure. To liberate the thiophene from its sulphonate, convert the latter into its lead salt, and decompose this by distilling it with ammonium chloride (*Berichte*, 17, 792). Or the thiophene sulphonic acid is mixed with water and distilled in a current of steam (*Berichte*, 18, 497).

All the thiophene present in crude benzene can be removed from it as dibromthiophene, $C_4H_2Br_2S$, by the addition of a little bromine (*Berichte*, 18, 1490).

To obtain thiophene from succinic acid heat a mixture of sodium succinate (100 gr.) and P_2S_3 (100 gr.) in a retort over the direct flame until the reaction sets in. The thiophene is expelled from the distillate when the latter is heated upon a water bath (*Berichte*, 18, 454).

Thiophene is a colorless liquid, with an odor resembling that of benzene. It boils at 84°. Its sp. gr. is 1.062 at 23°. It becomes crystalline when exposed to a mixture of solid carbon dioxide and ether. Sodium has no effect upon it even when it is heated. Mixed with a little sulphuric acid and isatin it becomes dark blue in color. The same occurs when its solution in sulphuric acid is added to phenanthraquinone in glacial acetic acid (Reaction of Laubenheimer, *Berichte*, 19, 673). All the dicarbonyl compounds, CO.CO, like benzil, alloxan, etc., behave the same as phenanthraquinone (*Berichte*, 16, 2962).

THIOPHENE HOMOLOGUES.

In these compounds the hydrogen of thiophene has been replaced by alkyls. They may be obtained by the action of alkyl iodides and metallic sodium upon iodothiophene (analogous to Fittig's synthesis of the benzenes) (*Berichte*, 17, 1559):—

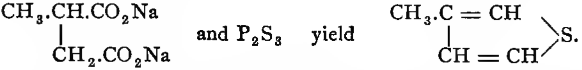
$$C_4H_3IS + C_2H_5I + 2Na = C_4H_3(C_2H_5)S + 2NaI.$$

Only the methylated thiophenes occur already formed in coal tar oil. They correspond fully to the homologous benzenes, and with isatin and phenanthraquinone yield colors similar to those obtained with thiophene.

1. **Methyl Thiophenes, Thiotolenes,** $C_4H_3S.CH_3$.

α-**Thiotolene,** $C_4H_3S.CH_3$, containing the methyl group in the α-position (p. 523), is produced from iodothiophene by the aid of methyl iodide and sodium, and from lævulinic acid by the action of P_2S_3 (p. 529). It boils at 126°, and is converted into α-thiophenic acid by oxidation.

β-**Thiotolene,** $C_4H_3S.CH_3$, is formed when sodium pyrotartrate is heated with P_2S_3 (*Berichte* 18, 454):—



$$\begin{array}{l}CH_3.CH.CO_2Na\\ \quad |\\ \quad CH_2.CO_2Na\end{array} \text{ and } P_2S_3 \text{ yield } \begin{array}{l}CH_3.C = CH\\ \qquad |\\ \qquad CH = CH\end{array}\!\!\Big> S.$$

It boils at 113°.

It becomes β-thiophenic acid when oxidized.

Both thiotolenes occur in coal tar (in toluene), and may be isolated from it in the same manner that thiophene is extracted. Formerly their mixture was considered a distinct thiotolene, as the tribromthiophene and the thiophenic acid, obtained from it appeared to differ from the corresponding α- and β-thiophene derivatives. Later research has shown it to be a mixture (*Berichte*, 18, 3005).

2. **Dimethyl Thiophene, Thioxene,** $C_4H_2S(CH_3)_2$.

(1, 2)-**Dimethyl Thiophene** is obtained from β-methyl-lævulinic acid, $CH_3.CO.CH(CH_3).CH_2.CO_2H$, by the action of P_2S_3 (p. 529). It boils at 136°, and is oxidized to (1, 2)-thiophene-dicarboxylic acid by potassium permanganate.

(1, 3)-**Dimethyl Thiophene** is formed when P_2S_3 acts upon α-methyl-lævulinic acid (p. 529). It is an oil, boiling at 137–138°. It gives an emerald green coloration with isatin. Alkaline permanganate oxidizes it to (1, 3)-thiophene-dicarboxylic acid.

(1, 4)-**Dimethyl Thiophene** is *Thioxene*, obtained from xylene. It may be synthesized by acting upon α-iodothiotolene with methyl iodide and sodium. It is also formed when P_2S_3 acts upon acetonyl acetone (p. 329). It boils at 135°, yields a cherry-red color with isatin, and with phenanthraquinone, etc., a violet coloration. Potassium permanganate oxidizes it to (1, 4)-thiophene-dicarboxylic acid.

(2, 3)-**Dimethyl Thiophene** has been obtained from symmetrical dimethyl-succinic acid by the action of P_2S_3. It boils at 145° (*Berichte*, 21, 1836).

α-**Ethyl Thiophene,** $C_4H_3S.C_2H_5$, from α-iodo- or brom-thiophene by means of ethyl bromide and sodium, is very similar to ethyl benzene. It boils at 132–134°. Permanganate oxidizes it first to thiēnylglyoxylic acid, and then to α-thiophenic acid.

β-**Ethyl Thiophene,** $C_4H_3S.C_2H_5$, is produced upon heating ethyl succinic acid with P_2S_3. It is perfectly similar to the α-compound, but yields β-thiophenic acid when oxidized (*Berichte*, 19, 3284).

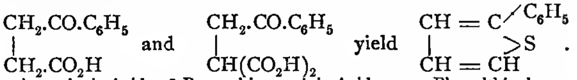
Trimethyl Thiophene, $C_4H(CH_3)_3S$, has been obtained from dimethyl-lævulinic acid by the action of P_2S_5 (*Berichte*, 20, 2085).

α-**Normal Propyl Thiophene,** $C_4H_3S.C_3H_7$, boils at 158°, and yields α-thiophenic acid when oxidized (*Berichte*, 20, 1740). **Isopropyl Thiophene,** $C_4H_3S.C_3H_7$, is prepared by the action of aluminium chloride upon thiophene and isopropylbromide. Sodium will not answer in this reaction. It boils at 154°. Unlike all other homologous thiophenes it yields an intense violet color directly with phenanthraquinone (*Berichte*, 19, 673).

Tetramethyl Thiophene, $C_4S(CH_3)_4$, is obtained from iodo-trimethyl thiophene by the action of methyl iodide and sodium. It boils about 183° (*Berichte*, 21, 1838).

α-**Methyloctyl Thiophene,** $C_4H_2S\left(\begin{matrix}CH_3\\C_8H_{17}\end{matrix}\right)$ (1, 4), from α-methylthiophene, is identical with that obtained from α-octylthiophene. This is proof of the *similarity of the two α-positions* (1) and (4) in thiophene (*Berichte*, 19, 649).

α-Phenylthiophene, $C_4H_3S.C_6H_5$, is prepared by heating β-benzoyl propionic acid or β-benzoylisosuccinic acid with P_2S_5 or P_2S_3:—



β-Benzoyl-propionic Acid. β-Benzoyl-isosuccinic Acid. α-Phenylthiophene.

The product crystallizes from alcohol in small plates, melting at 40–41° (*Berichte*, 19, 3140).

Methylphenyl Thiophene, $C_4H_2S<^{CH_5}_{C_6H_5}$. The (1, 4)-compound results from the action of P_2S_5 upon acetophenon-acetone, $C_6H_5.CO.CH_2\ CH_2.CO.CH_3$. It melts at 51° and boils at 270°. (1, 3)-**Methylphenyl thiophene**, from α-phenyllævulinic acid and P_2S_3 (p. 529), melts at 73° (*Berichte*, 20, 2558).

HALOGEN DERIVATIVES.

Chlorine and bromine attack thiophene in the cold. The action is even more energetic than with the benzenes. Iodine, in the presence of mercuric oxide (p. 91), also attacks it at the ordinary temperature. The three halogens first enter the α-position. In properties the haloid thiophenes are very similar to the benzene haloids.

α-Chlorthiophene, C_4H_3ClS, boils at 130°, and **Dichlorthiophene**, $C_4H_2Cl_2S$, at 170°. **Tetrachlorthiophene**, C_4Cl_4S, melts at 36°, and boils from 220–240°. When thiophene is brominated, even in the cold, the chief product is the dibromide. A little of the monobromide is formed at the same time.

α-Bromthiophene, C_4H_3BrS, boils at 150°. It yields α-ethylthiophene, when acted upon by ethyl iodide and sodium. (1, 4)-**Dibromthiophene**, $C_4H_2Br_2S$, boils at 211°. Its formation serves for the complete isolation of all the thiophene that may be present in a thiophene-benzene (*Berichte*, 18, 1490). **Tribromthiophene**, C_4HBr_3S, melts at 29°, and boils at 260°. **Tetrabromthiophene**, C_4Br_4S, is the final product in the bromination of thiophene. It crystallizes in brilliant needles, that melt at 112°, and boil at 326°.

α-Iodo-thiophene, C_4H_3IS, is obtained from thiophene by the action of iodine and mercuric oxide, even in the cold. It is a liquid and boils at 182°. Chlorcarbonic ester and sodium convert it into α-thiophene carboxylic acid. **Diiodothiophene**, $C_4H_2I_2S$, melts at 40°.

NITRO-DERIVATIVES.

The action of nitric acid upon thiophene is so very energetic that in order to moderate the reaction air charged with thiophene vapor is conducted into the fuming nitric acid. Mono- and dinitrothiophene are then produced (*Berichte*, 17, 2648).

Nitrothiophene, $C_4H_3(NO_2)S$, is quite similar to paranitrotoluene. From cold solutions it separates in bright yellow prisms, melting at 44° and boiling at 225°. Its odor resembles that of nitrobenzene.

Dinitrothiophene, $C_4H_2(NO_2)_2S$, resembles dinitrobenzene. It melts at 52° and boils at 290°. It is volatile with steam. Caustic potash colors its alcoholic solution dark red. The same coloration of dinitrobenzene, caused in the same way, is due to admixed dinitrothiophene (*Berichte*, 17, 2778). When repeatedly distilled with water dinitrothiophene is converted into a modification, melting at 78°.

AMIDO-DERIVATIVES.

Nitrothiophene is reduced with much more difficulty than the nitrobenzenes. The reduction succeeds when zinc and hydrochloric acid are allowed to act upon the dilute alcoholic solution (*Berichte*, 18, 1490).

Amidothiophene, Thiophenin, $C_4H_3S.NH_2$, analogous to aniline, is a bright yellow oil. It rapidly resinifies on exposure to the air. Its HCl-salt consists of deliquescent needles. It does not yield a diazo-derivative when acted upon with nitrous acid. It combines immediately with salts of diazobenzene, forming stable, mixed azo-dyestuffs, *e. g.*, $C_6H_5.N:N—C_4H_2S.NH_2.HCl$ (*Berichte*, 18, 2316).

SULPHO-ACIDS.

Like the benzene sulphonic acids, the thiophene sulpho-derivatives are produced by dissolving thiophene in sulphuric acid, generally at the ordinary temperature. They can also be prepared from the thionyl-ketones (p. 534) (*Berichte*, 19, 674, 2623):—

$$C_4H_3S.CO.CH_3 + SO_4H_2 = C_4H_3S.SO_3H + CH_3.CO_2H.$$

α-Thiophene Sulphonic Acid, $C_4H_3S.SO_3H$, is formed upon shaking thiophene with ordinary sulphuric acid (*Berichte*, 19, 1615). The acid, liberated by hydrogen sulphide from its lead salt, consists of very deliquescent crystals. If it be distilled it yields thiophene. Its derivatives are perfectly analogous to those of benzene-sulphonic acid.

β-Thiophene Sulphonic Acid, $C_4H_3S.SO_3H$, is obtained when sodium amalgam acts upon α-dibrom-thiophene sulphonic acid. It is very similar to the α-acid.

(1, 4)-Thiophene Disulphonic Acid, $C_4H_2S(SO_3H)_2$, is produced by the action of fuming sulphuric acid upon the α-mono-sulphonic acid, while **(2, 3)-Thiophene Disulphonic Acid,** $C_4H_2S(SO_3H)_2$, is obtained by reducing α-dibromthiophene-disulphonic acid, $C_4Br_2S(SO_3H)_2$, with sodium amalgam (*Berichte*, 19, 184).

The sulphonic acids of the homologous thiophenes cannot be prepared by sulphonating the latter, but are derived from their ketone compounds. Thus, methylthiënyl-methyl-ketone yields **Methylthiophen-sulphonic Acid,** $C_4H_2(CH_3)S.SO_3H$ (*Berichte*, 19, 1620):—

$$C_4H_2(CH_3)S.CO.CH_3 + SO_4H_2 = C_4H_2(CH_3)S.SO_2H + CH_3.CO_2H.$$

PHENOLS.

α Oxythiophene, $C_4H_3S.OH$, is not known. **Thiënylsulphydrate,** $C_4H_3S.SH$, corresponding to it, is prepared by reducing α-thiophene-sulphonic chloride, $C_4H_3S.SO_2Cl$, with zinc and hydrochloric acid. It is present in the crude thiophene product obtained by distilling succinic acid with P_2S_5. It is a yellow oil, with a very unpleasant odor. It boils about 166°. It unites with benzene diazo-compounds to form azo-dyestuffs. Phenol does not show this reaction (*Berichte*, 19, 1617).

α-Oxymethylthiophene, Oxythiotolene, $C_4H_2(CH_3)S.OH(1, 4)$, is synthetically prepared by heating lævulinic acid with P_2S_5. If P_2S_3 be employed the oxythiotolene will be further reduced to α-thiotolene (p. 531). It is a colorless oil, with a disagreeable odor. It boils about 200°. It is soluble in alkalies. Carbonic acid again separates it (*Berichte*, 19, 555).

ALDEHYDES AND KETONES.

α-**Thiophen-Aldehyde,** $C_4H_3S.CHO$, results from the distillation of thiënyl-glyoxylic acid, $C_4H_3S.CO.CO_2H$ (*Berichte*, 19, 1885). It is a yellow oil, with an odor resembling that of benzaldehyde, $C_6H_5.CHO$. It boils at 198°. It has all the properties of an aldehyde. It reacts with fuchsine-sulphurous acid and diazobenzenesulphonic acid (p. 189); combines with hydroxylamine to *thiophenaldoxime* and with phenylhydrazine to *thiophenalhydrazone*, $C_4H_3S.CH(N_2H.C_6H_5)$, melting at 119° (*Berichte*, 19, 637; 1854). Thiophenaldehyde, like benzaldehyde, condenses with dimethyl aniline, forming a green dye, corresponding to malachite green.

If oxidized, even in the air, it forms α-thiophenic acid. Aqueous caustic potash converts it into thiophenic acid and thiophene alcohol: $2C_4H_3S.CHO + KOH = C_4H_3S.CO_2K + C_4H_3S.CH_2.OH$.

α-**Thiophene Alcohol**, $C_4H_3S.CH_2.OH$, thiënyl carbinol, is an aromatic liquid, boiling at 207°. It is perfectly analogous to benzyl alcohol, $C_6H_5.CH_2.OH$.

The ketone derivatives of thiophene are obtained in the same manner as those of the benzene series, viz., by the action of acid chlorides upon thiophene in the presence of aluminium chloride (reaction of Friedel) (*Berichte*, 17, 2643):—

$$C_4H_4S + C_2H_3OCl = C_4H_3S.CO.CH_3 + HCl.$$

α-**Thiënyl-methyl Ketone**, $C_4H_3S.CO.CH_3$, Acetothiënone, the analogue of acetophenone, $C_6H_5.CO.CH_3$, is obtained from thiophene and acetyl chloride by means of aluminium chloride. It is an oil, boiling at 213°. Its odor resembles that of acetophenone. Being a ketone, it unites with both hydroxylamine and phenylhydrazine. If it be oxidized with permanganate, it first forms thiophene glyoxylic acid, $C_4H_3S.CO.CO_2H$, and then α-thiophenic acid (*Berichte*, 19, 2115).

Methyl thiënyl-methyl ketone, $C_4H_2(CH_3)S.CO.CH_3$, acetyl thiotolene, from α-methyl thiophene and acetyl chloride, boils at 216°.

Acetyl thioxene, $C_4H(CH_3)_2S.CO.CH_3$, from thioxene and acetyl chloride, boils at 224°. It yields thiophene tricarboxylic acid when oxidized with permanganate.

When these ketones are heated with concentrated sulphuric acid, the acid radical breaks off, and thiophene sulphonic acids are produced (p. 533). If, however, SO_3 or pyrosulphuric acid be allowed to act in the cold upon the ketones, then the products will be ketone-sulphonic acids (*Berichte*, 19, 2624).

Thiënyl Cyanide, $C_4H_3S.CN$, Thiophene nitrile, is obtained by distilling potassium thiophen-sulphonate with potassium cyanide or yellow prussiate of potash. It is perfectly similar to benzonitrile (phenylcyanide), and is an oil, having an odor very similar to that of oil of bitter almonds. It boils at 190°.

THIOPHENE CARBOXYLIC ACIDS.

Thiophene carboxylic acids are formed by methods which are perfectly analogous to those employed in the preparation of the aromatic acids:—

(1) By the oxidation of the homologous thiophenes with a solution of alkaline potassium permanganate (*Berichte*, 18, 546). The side chains are thus converted into carboxyl groups. Ethyl-thiophene first yields thiophene-glyoxylic acid, $C_4H_3S.CO.CO_2H$, but

this changes to thiophenic acid. The thiophene ketones, under similar treatment, yield first ketonic acids and then carboxylic acids (*Berichte* 18, 537).

(2) By the action of chlor-carbonic ester and sodium amalgam upon iodo- or brom- thiophene:—

$$C_4H_3IS + ClCO_2.C_2H_5 + 2Na = C_4H_3S.CO_2.C_2H_5 + NaCl + NaI.$$

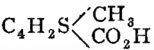
The thiophene carboxylic acids are perfectly similar to the benzene carboxylic acids in external properties and reactions. They split off carbon dioxide and revert to thiophene, $C_4H_3S.CO_2H = C_4H_4S + CO_2$, when distilled with lime.

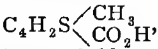
α-**Thiophene Carboxylic Acid,** $C_4H_3S.CO_2H$, is formed when α-ethyl thiophene is oxidized with potassium permanganate; when chlorcarbonic ester and sodium act upon mono- or di-iodo-thiophene (*Berichte*, 18, 2304); and upon heating mucic acid with barium sulphide (p. 522), when carbon dioxide is expelled. The acid is very similar to benzoic acid; it crystallizes from hot water in flat needles, melts at 126.5°, and boils at 260°. It is very volatile in a current of steam. Its vapors, like those of benzoic acid, produce coughing. Its *ethyl ester*, $C_4H_3S.CO_2.C_2H_5$, boils at 218°.

β-**Thiophene Carboxylic Acid,** $C_4H_3S.CO_2H$ (2 = 3), is produced when β-methyl thiophene is oxidized with potassium permanganate (*Berichte*, 18, 3003; 19, 3284). It crystallizes from water in thick needles. It volatilizes very readily in a current of steam. It sublimes in leaflets, and melts at 136°.

If two parts of the α-acid and 1 part of the β-acid be crystallized together, homogeneous needles separate. These melt constantly at 116–117°, and cannot be resolved into their components again by fractional crystallization (*Berichte*, 19, 2891). The same compound, melting at 118°, is produced when crude thiotolene (from α- and β-thiotolene, p. 531) is oxidized (*Berichte*, 18, 548), and when thiophen-nitrile, $C_4H_3S.CN$ (from thiophene sulphonic acid, p. 533), is saponified with alcoholic potash. It was formerly thought to be a peculiar isomeric thiophene carboxylic acid and bore the name of α-thiophene carboxylic acid (*Annalen*, 236, 200).

METHYL-THIOPHENIC ACIDS.

α-**Methyl Thiophenic Acid,**  $C_4H_2S\begin{cases}CH_3\\CO_2H\end{cases}$ (1, 4), α-Thiotolenic Acid, is prepared by the action of chlorcarbonic ester and sodium amalgam upon mono- and di-iodo-thiotolene (*Berichte*, 18, 2304; 19, 656), as well as by the oxidation of synthetic thioxene with a permanganate solution. A little of the dicarboxylic acid is formed simultaneously (*Berichte*, 18, 2254). It melts at 137° (142°), and passes into the corresponding dicarboxylic acid when further oxidized.

β-**Methyl Thiophenic Acid,**  $C_4H_2S\begin{cases}CH_3\\CO_2H\end{cases}$, β-Thiotolenic Acid, results from the interaction of β-iodothiophene and chlorcarbonic ester (*Berichte*, 19, 657), and by the oxidation of acetyl-β-thiotolene, $C_4H_2S(CH_3).CO.CH_3$. It melts at 144°. It does not yield a dicarboxylic acid when further oxidized (*Berichte*, 19, 680).

α-Thiënyl-acetic Acid, $C_4H_3S.CH_2.CO_2H$, results upon reducing α-thiënylglycollic acid by digesting it with hydriodic acid and phosphorus. It dissolves with difficulty in water, and melts at 76°.

α-Ethyl Thiophenic Acid, $C_4H_2(C_2H_5)S.CO_2H$ (1, 4), is obtained from iodoethyl thiophene and chlorcarbonic ester. It melts at 71°.

Keton-Acids and Oxy-Acids.

α-Thiënylglyoxylic Acid, $C_4H_3S.CO.CO_2H$, is obtained by carefully oxidizing acetyl thiophene, or ethyl thiophene, with permanganate (*Berichte*, 18, 537; 19, 2115). It is a crystalline mass, readily soluble in water, and when perfectly anhydrous it melts at 91.5°. It decomposes into carbon dioxide and thiophenaldehyde when heated.

See *Berichte*, 20, 1746, upon three isomeric methylthiënylglyoxylic acids.

Sodium amalgam converts thiënylglyoxylic acid into

Thiënylglycollic Acid, $C_4H_3S.CH(OH).CO_2H$, corresponding to mandelic acid, $C_6H_5.CH(OH).CO_2H$. It is very soluble in water and melts at 115° (*Berichte*, 19, 3281).

POLYCARBONIC ACIDS.

Thiophene Dicarboxylic Acids, $C_4H_2S.(CO_2H)_2$. Four acids of this class are possible; three of these are known.

The *(1, 2)-acid*, obtained by oxidizing (1, 2)-thioxene with permanganate, decomposes if it be heated above 260°. Like phthalic acid, it forms a fluoresceïn with resorcinol.

The *(1, 3)-acid*, from (1, 3)-thioxene, is volatile with steam, and crystallizes from hot water in thin needles, melting at 118°. The *(1, 4)-acid* is prepared as follows:—

(1) By oxidizing (1, 4)-thioxene, α-methyl- and α-ethyl-thiophenic acid, and acetyl-ethyl thiophene (p. 534) with permanganate (*Berichte*, 19, 3275); (2) From α-thiophene disulphonic acid by means of the dicyanide (*Berichte*, 19, 491); and (3) From dibromthiophene and chlor-carbonic ester. It dissolves with great difficulty in cold water. It is a crystalline powder, that sublimes without melting, at a temperature above 300°. In most of its properties it resembles terephthalic acid, $C_6H_4(CO_2H)_2$ (1, 4). Sodium amalgam reduces it to

Tetrahydro-thiophene Dicarboxylic Acid, $C_4H_6S(CO_2H)_2$. This compound dissolves readily in cold water, and melts at 162°. It reduces ammoniacal solutions, especially upon warming. When heated with sulphuric acid it evolves carbon monoxide and sulphur dioxide. In this respect it resembles the hydrophthalic acids (*Berichte*, 19, 3274).

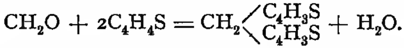
Thiophene Carboxylic Acid, $C_4HS(CO_2H)_3$, is obtained by oxidizing acetylthioxene with potassium permanganate. Its *trimethyl ester* crystallizes from alcohol in leaflets, melting at 118° (*Berichte*, 18, 2303).

Thiënyl Acrylic Acid, $C_4H_3S.CH:CH.CO_2H$, contains an unsaturated side-group. It is analogous to cinnamic acid. Like the latter it can be prepared from thiophene aldehyde, by means of sodium acetate and acetic anhydride (see furfuracrylic acid). It crystallizes from hot water in needles, melting at 138° (*Berichte*, 19, 1856).

CONDENSED THIOPHENE DERIVATIVES.

Dithiënyl, $C_4H_3S.C_4H_3S$, corresponding to diphenyl, $C_6H_5.C_6H_5$, is produced when thiophene vapors are conducted through a tube heated to redness. It is quite similar to diphenyl, crystallizes in bright leaflets, that melt at 83° and boil at 266°.

Thiophene condenses with the aldehydes of the marsh gas series, forming compounds quite analogous to the diphenyl-methane compounds :—



$$CH_2O + 2C_4H_4S = CH_2\begin{cases}C_4H_3S\\C_4H_3S\end{cases} + H_2O.$$

Dithiēnyl Methane, $C_4H_3S.CH_2.C_4H_3S$, from thiophene and methylal (p. 301) by the action of sulphuric acid, is an oil with the odor of oranges. It boils at 267°. It solidifies when cooled, and melts at 43°.

Dithiēnyl Trichlor-ethane, $(C_4H_3S)_2CH.CCl_3$, from thiophene and chloral, $HOC.CCl_3$, forms plate-like crystals, melting at 76°.

Thiēnyl-phenyl Methane, $C_4H_3S.CH_2.C_6H_5$, is obtained by the action of sulphuric acid upon thiophene and benzyl alcohol, $C_6H_5.CH_2.OH$. It is an oil, boiling at 265°. It has a fruity odor.

Dithiēnyl Ketone, $C_4H_3S.CO.C_4H_3S$, Thiēnone, is perfectly similar to benzophenone, $(C_6H_5)_2CO$, and is produced by analogous methods: by the action of phosgene upon thiophene in the presence of aluminium chloride (*Berichte*, 18, 3012): $COCl_2 + 2C_4H_4S = CO(C_4H_3S)_2 + 2HCl$; and by the distillation of calcium α-thiophenate. It crystallizes from alcohol in needles or leaflets, melting at 88° and boiling at 326°.

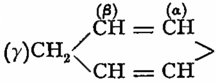
Thiēnyl-phenyl Ketone, $C_4H_3S.CO.C_6H_5$, is obtained from thiophene and benzoyl chloride by the aid of aluminium chloride: $C_4H_4S + C_6H_5.COCl = C_4H_3S.CO.C_6H_5 + HCl$. It melts at 55°, and boils about 360°. When heated with lime, it decomposes into thiophene and benzoic acid.

Thiēnyl-diphenyl Methane, $C_4H_3S.CH\begin{cases}C_6H_5\\C_6H_5\end{cases}$, is produced by the condensation of thiophene and benzhydrol, $(C_6H_5)_2CH.OH$, by means of P_2O_5. It crystallizes in white leaflets, that melt at 63° and boil about 335° (*Berichte*, 19, 1624).

The higher, condensed thiophene derivatives, as **Thionaphtene**, C_8H_6S, and **Thiophtene**, $C_6H_4S_2$, will be discussed with the corresponding benzene derivatives.

PENTHIOPHENE DERIVATIVES.

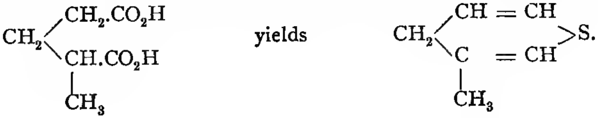
A ring of four carbon atoms linked to or closed by sulphur, exists (same in the γ-lactone ring) in the thiophene nucleus. *Penthiophene* is an analogous parent nucleus. In it there is a chain of five carbon atoms closed by sulphur (similar to the δ-lactones):—



Penthiophene.

But very few derivatives are known.

β-Methyl-penthiophene, $C_5H_5S.CH_3$, is prepared like thiophene from succinic acid, by heating sodium α-methyl glutarate with P_2S_3 (*Berichte*, 19, 3266):—



It is a strongly refracting oil, boiling at 134°. Its specific gravity is 0.994 at 19°. Sodium does not affect it. It resembles thiophene very much in all of its reactions. It yields a dark green color with isatin and sulphuric acid, and a violet coloration with phenanthraquinone. Acetyl chloride and aluminium chloride convert it into:—

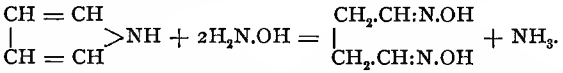
Methylpenthiophene-methyl Ketone, $C_5H_4(CH_3)S.CO.CH_3$, acetyl-methylpenthiophene. This is a heavy oil, resembling acetophenone, $C_6H_5.CO.CH_3$, in odor. It boils about 235°. It forms a *ketoxime* with hydroxylamine; this compound melts at 68°.

The penthiophene ring is less stable than that of thiophene. Methyl penthiophene is completely oxidized by dilute permanganate even in the cold.

PYRROL GROUP.

In pyrrol, C_4H_5N, there is a chain of four carbon atoms closed by nitrogen. The latter is combined with an atom of hydrogen, thus forming the imide group (p. 521). The pyrrols, consequently manifest a feeble basic nature; they gradually dissolve in acids, but do not form salts with them, as they are resinified. The constitution of pyrrol and its relations to furfurane and thiophene are deduced from its analogous syntheses from the γ- or (1, 4)-dicarbonyl compounds. These will be more fully discussed later under the individual groups (pp. 544, 545).

A rather remarkable occurrence is the reversal of these syntheses, *i. e.*, the decomposition of the pyrrol ring with elimination of the imide group. This is induced by the action of hydroxylamine. Dioximes are thus produced. Thus, pyrrol yields succindialdoxime (p. 325) (*Berichte*, 22, 1968);—

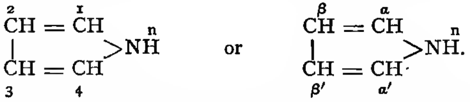


$$\left.\begin{array}{l}CH = CH\\ |\\ CH = CH\end{array}\right> NH + 2H_2N.OH = \begin{array}{l}CH_2.CH:N.OH\\ |\\ CH_2.CH:N.OH\end{array} + NH_3.$$

(1, 4)-Dimethyl pyrrol yields the dioxime of acetonyl acetone (p. 328) in a similar manner.

(1, 3)-Dimethyl pyrrol, (1, 4)-methyl-phenyl pyrrol, and *n*-ethyl pyrrol react similarly, while *n*-phenyl pyrrol, (1, 4)-diphenyl pyrrol, etc., do not (*Berichte*, 23, 1792).

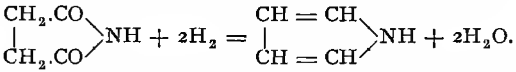
The possible isomeric derivatives of pyrrol may be deduced from the following symbols:—



$$\left.\begin{array}{l}\overset{2}{CH} = \overset{1}{CH}\\ |\\ \underset{3}{CH} = \underset{4}{CH}\end{array}\right> \overset{n}{NH} \quad \text{or} \quad \left.\begin{array}{l}\overset{\beta}{CH} = \overset{\alpha}{CH}\\ |\\ \underset{\beta'}{CH} = \underset{\alpha'}{CH}\end{array}\right> \overset{n}{NH}.$$

The positions 1 and 4 are equal in value; they are called the α-positions. 2 and 3 are also alike, and are termed the β-positions. Consequently, the mono-derivatives of pyrrol (those in which the CH-groups suffer substitution) occur in two modifications—the α- and β. There are four di-derivatives, $C_4H_2R_2(NH)$. Those in which the two α-positions are replaced, will be termed in the following pages, *a* or (1, 4)-derivatives, and the $\beta\beta'$-compounds will be called β- or (2, 3) derivatives, etc. The compounds formed by the replacement of the hydrogen of the NH-groups, will be called *N*- or *n*-derivatives.

Pyrrol, $C_4H_4{:}NH$, was first found in coal tar and bone oil. It received its name from its property of imparting a red color to a pine shaving, moistened with hydrochloric acid. It is produced when acetylene and ammonia are conducted through tubes heated to redness: $2C_2H_2 + NH_3 = C_4H_4NH + H_2$; and by the distillation of ammonium saccharate or mucate, or upon heating glycerol to 200°. Its formation upon heating succinimide (p. 412) with zinc dust containing zinc hydroxide, is very interesting:—



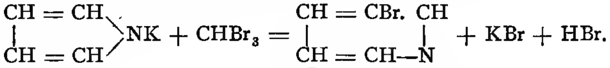
$$\begin{array}{l}CH_2.CO\\ \vert\\ CH_2.CO\end{array}\!\!>NH + 2H_2 = \begin{array}{l}CH = CH\\ \vert\\ CH = CH\end{array}\!\!>NH + 2H_2O.$$

It also results if pyroglutaminic acid be heated (p. 467). Tetrachlorpyrrol, C_4Cl_4NH (*Berichte*, 19, 3027), is produced in an analogous manner from dichlormaleïmide (p. 428).

Preparation.—Shake bone oil with dilute sulphuric acid (1 : 30) to remove all basic substances (pyridine bases). The residual oil contains nitriles of the fatty acids (from propionic to stearic acid), which are saponified upon boiling them with caustic potash, and in addition benzene hydrocarbons, pyrrol and its homologues (*Berichte*, 13, 65). The oil obtained in the distillation of bone-glue (free from fats) contains large quantities of pyrrols, with a little pyrocoll (*Berichte*, 14, 1108). To isolate the pyrrol that portion of the purified oil boiling at 115–130° is treated with metallic potassium, whereupon solid potassium-pyrrol, C_4H_4NK (see below), separates. It can also be obtained by boiling the pyrrol with solid caustic potash (*Berichte*, 19, 173). The potassium-pyrrol is washed with ether, decomposed by water, and the oil distilled over in a current of steam. It is then dried over fused caustic potash and fractionated.

Pyrrol is a colorless liquid with an odor resembling that of chloroform. It becomes brown upon exposure and boils at 131°. Its sp. gr. is 0.9752 at 12.5°. It is but slightly soluble in water, but dissolves very readily in alcohol and ether. A pine shaving, moistened with hydrochloric acid, is colored a pale red by its vapors. This increases to an intense carmine red. It yields an indigo blue coloration with isatin and sulphuric acid, or with phenanthraquinone, etc. (p. 521) (*Berichte*, 17, 142, 1034; 19, 106). Pyrrol is a very feeble base. It is dissolved very slowly in the cold by dilute acids, but does not yield salts (*Berichte*, 21, 1478). When heated it passes into a red powder, *pyrrol red*, $C_{12}H_{14}N_2O$, which becomes brown on exposure. Nitric acid resinifies pyrrol and oxidizes it to oxalic acid.

The conversion of pyrrol into chlor- and brom-pyridine upon heating potassium-pyrrol, or pyrrol and sodium alcoholate, with chloroform or bromoform, etc. (see pyridine), is rather interesting :—



$$\left.\begin{matrix}CH = CH\\ | \\ CH = CH\end{matrix}\right\rangle NK + CHBr_3 = \begin{matrix}CH = CBr.\ CH\\ | \qquad\qquad\quad | \\ CH = CH—N\end{matrix} + KBr + HBr.$$

Brom-pyridine.

Pyrrol is a secondary amine. The hydrogen of its NH-group can be replaced by potassium (not sodium), acid radicals, and alkyls.

Potassium dissolves in pyrrol with an energetic evolution of hydrogen. It forms **Potassium-pyrrol**, C_4H_4NK, a crystalline mass. This compound may also be obtained by boiling pyrrol with solid caustic potash (*Berichte*, 19, 173). Water regenerates pyrrol and caustic potash. Sodium will only act upon pyrrol when they are heated together under pressure.

***n*-Acetyl Pyrrol**, $C_4H_4N.CO.CH_3$, is produced (together with pyrrol-methyl-ketone) upon heating pyrrol with acetic anhydride. A simpler procedure consists in treating potassium-pyrrol with acetyl chloride. It is an oil with peculiar odor. It boils at 178°. It is decomposed into pyrrol and acetic acid when it is digested with caustic potash. Hydrochloric acid converts it into a resin.

Cyan Pyrrol, $C_4H_4N.CN$, is produced in the action of cyanogen chloride upon potassium-pyrrol. It rapidly polymerizes to a melamine derivative. In this respect it resembles cyanamide (p. 288).

***n*-Pyrrol Carboxylic Ester**, $C_4H_4N.CO_2.C_2H_5$, Pyrrol Urethane, corresponding to ordinary urethane, is formed when chlor-carbonic ester acts upon potassium-pyrrol (p. 382). It is an oil boiling at 180°. Boiling alkalies separate it into its components. It passes into **Pyrrol Carbamide**, $C_4H_4N.CO.NH_2$, if it is heated with aqueous ammonia. This is a crystalline compound that melts at 166°, and volatilizes without decomposition.

Phosgene, $COCl_2$, converts potassium-pyrrol into **Carbonyl Pyrrol**, $CO\left\langle\begin{matrix}N.C_4H_4\\N.C_4H_4\end{matrix}\right.$ (together with the isomeric dipyrryl ketone, p. 545). This compound consists of large crystals, melting at 63°, and distilling at 238°. When heated in a tube to 250°, it is converted into isomeric dipyrryl ketone, $CO\left\langle\begin{matrix}C_4H_3.NH\\C_4H_3.NH\end{matrix}\right.$ (*Berichte*, 18, 1828).

n-Alkyl Derivatives.

The alkylic pyrrols, $C_4H_4{:}NR$, containing the alkyl group in union with the nitrogen atom, correspond to the ordinary amines (p. 157), and are called *N*- or *n*-alkyl pyrrols. The homologous pyrrols are isomeric with the preceding. They contain the alkyls attached to carbon (p. 542). The *n*-alkyl pyrrols are produced by the action of the alkyl iodides upon potassium-pyrrol, C_4H_4NK;

also in the distillation of the amine salts of mucic and saccharic acids, as well as by heating the alkylic succinimides, $C_4H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle NR$ (p. 413), with zinc dust. The *n*-alkyl pyrrols are quite similar to pyrrol. They yield intense colorations with isatin and phenanthraquinone. They are not so easily resinified by acids as the pyrrols.

n-**Methyl Pyrrol**, $C_4H_4N.CH_3$, boils at 113°; its sp. gr. is 0.9203 at 10°. *n*-**Ethyl Pyrrol**, $C_4H_4N.C_2H_5$, boils at 131°; its sp. gr. is 0.9042 at 10°. A pine shaving, moistened with hydrochloric acid, is colored an intense red by its vapors. Ethylamine is liberated when it is boiled with hydrochloric acid. Potassium does not attack it. *n*-**Isoamyl Pyrrol**, $C_4H_4N.C_5H_{11}$, boils at 180–184°. *n*-**Allyl Pyrrol**, $C_4H_4N.C_3H_5$, from potassium-pyrrol and allyl iodide, can be distilled under reduced pressure.

n-**Phenyl Pyrrol**, $C_4H_4N.C_6H_5$, from aniline mucate and saccharate, consists of brilliant scales, having a camphor-like odor. They assume a red color on exposure to the air, and melt at 62°.

SUBSTITUTED PYRROLS.

Tetrachlor-pyrrol, C_4Cl_4NH, is produced by acting upon dichlomaleïmide with phosphorus pentachloride (p. 428), and when zinc and acetic acid act upon the perchloride of perchlorpyrocoll (p. 547). It crystallizes from benzine in colorless leaflets. These volatilize very readily and melt at 110° with decomposition.

Tetra-iodo-pyrrol, C_4I_4NH, **Iodol**, is formed when iodine acts upon pyrrol in the presence of some indifferent solvent, but more readily if substances are present that will absorb the liberated hydriodic acid (such as iodic acid, p. 91, or caustic alkalies, *Berichte*, **19**, 3027).

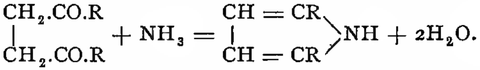
Iodol crystallizes in yellowish-brown prisms. These decompose about 140°. It is almost insoluble in water; 100 parts of 90 per cent. alcohol dissolve 5.8 parts at 15°. If small portions of it be carefully digested with sulphuric acid they will dissolve, and the solution acquire an intense green coloration, which subsequently becomes dirty violet. As tetra-iodo-pyrrol is odorless, but possesses the same action as iodoform, it has been substituted for the latter as an antiseptic, under the name of *iodol* (*Berichte*, **20**, Ref. 220).

Few pyrrol compounds can be directly nitrated. Nitric acid attacks them too violently.

Dinitro-pyrrol, $C_4H_2(NO_2)_2NH$, is obtained from pyrrol-methyl-ketone, $C_4H_3(CO.CH_3)NH$ (together with nitro-derivatives of the latter), by the action of cold fuming nitric acid, and by the nitration of α-pyrrol-carboxylic acid, $C_4H_3(NH).CO_2H$ (*Berichte*, **19**, 1078). It crystallizes from hot water in large yellow leaflets, melting at 152°. It behaves like an acid, dissolves in alkaline carbonates and forms yellow colored salts.

HOMOLOGOUS PYRROLS.

The *c*-alkyl pyrrol homologues contain the alkyls attached to carbon. When acted upon by potassium, or if boiled with solid caustic potash, they form potassium derivatives. This behavior distinguishes them from the isomeric *n*-alkyl pyrrols. In the preceding reaction the lower alkyl pyrrols react before the higher pyrrols (*Berichte*, 19, 2199). They occur already formed in bone oil. They are artificially prepared from the corresponding carbonic acids, which were built up synthetically. The latter lose carbon dioxide.(p. 545). Some of them have been directly synthesized from *γ*-diketones, *e. g.*, acetonyl acetone, $CH_3.CO.CH_2.CH_2.CO.CH_3$, and acetophenone acetone, $C_6H_5.CO.CH_2.CH_2.CO.CH_3$ (pp. 328, 522), by heating the latter with alcoholic ammonia:—



$$\begin{matrix}CH_2.CO.R\\ |\\ CH_2.CO.R\end{matrix} + NH_3 = \left.\begin{matrix}CH = CR\\ |\\ CH = CR\end{matrix}\right\rangle NH + 2H_2O.$$

The *c*-alkyl pyrrols are also produced together with the *n*-alkyl pyrrols (p. 540) by the action of the alkyl iodides upon potassium-pyrrol (*Berichte*, 22, 659). The *n*-alkyl pyrrols, when heated with alkyl iodides and potassium carbonate to 120–140°, are converted into *n*-*c*-alkyl pyrrols (*Berichte*, 22, 656, 2515). The H of CH is then directly replaced. If the heating be prolonged and intensified a simultaneous conversion of the *c*-alkyl pyrrols into basic pyridines occurs. The 'five-membered' pyrrol ring is converted into the pyridine ring, consisting of six members. The *c*-alkyl pyrrols sustain a similar conversion into pyridines when they are digested with concentrated hydrochloric acid (*Berichte*, 19, 2199). The change of the pyrrols, by hydrochloric acid, into derivatives of *indol*, depends upon analogous reactions (*Berichte*, 21, 3429; 22, 1924).

The *c*-alkyl indols resemble pyrrol, but are more stable towards acids. Their aqueous solutions yield a white, caseous precipitate when treated with a solution of corrosive sublimate.

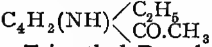
The possible isomerides of the alkyl pyrrols may be deduced from the scheme given upon p. 538. The mono-derivatives exist in two isomeric forms, the *α*- and *β*.

Methyl Pyrrols, $C_4H_3(NH).CH_3$, Homopyrrols. The *α*- and *β*-isomerides both occur in that fraction of Dippel's oil that boils from 140–150°. They cannot be separated. When carbon dioxide acts upon their potassium compound, two isomeric methyl-pyrrol-carboxylic acids, $C_4H_2(CH_3)(NH).CO_2H$, are produced. The pure methyl pyrrols result when these acids lose carbon dioxide. *α-Methyl pyrrol* boils at 148°, while the *β*-variety boils at 143°. They are more readily changed on exposure to the air than pyrrol. Oxidizing agents convert them into acetic acid and carbon dioxide. They pass into the corresponding pyrrolcarboxylic acids (*α*- and *β*-) when fused with caustic alkali. If a mixture of the two methylpyrrols be heated with acetic anhydride, *n*-acetyl-methyl pyrrol, $C_4H_3(CH_3)N.CO.CH_3$, and methyl pyrrol-methyl ketone, $C_4H_2\left(\begin{matrix}CH_3\\ C_2H_3O\end{matrix}\right)NH$ (*Berichte*, 19, 1408), are produced.

aa-**Dimethyl Pyrrol**, $C_4H_2(CH_3)_2NH(1, 4)$, is present in Dippel's oil. It is obtained from its mono- and di-carboxylic acids, when these lose carbon dioxide (*Berichte*, **23**, 1475). It may be synthesized by heating acetonyl acetone with alcoholic ammonia (p. 522). It is a colorless oil, boiling at 165°. It rapidly acquires a red color on exposure to the air. The colorations with isatin and phenanthraquinone are less intense (*Berichte*, **18**, 1566, 2254).

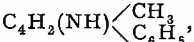
aβ-**Dimethyl Pyrrol** (1, 2) occurs in Dippel's oil. It boils at 165°. Hydrochloric acid converts it into tetramethyl indol (*Berichte*, **22**, 1923).

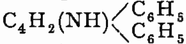
aβ'-**Dimethyl Pyrrol**, $C_4H_2(CH_3)_2NH(1, 3)$, results when its mono- and dicarboxylic acids (p. 548) lose carbon dioxide. It is an oil, with an odor resembling that of chloroform. It boils at 160°, and turns brown on exposure to the air (*Annalen*, **236**, 326).

Ethyl Pyrrol, $C_4H_3(C_2H_5)NH$, is produced by the action of zinc chloride upon a mixture of pyrrol and aldehyde: $C_4H_4NH + 2C_2H_4O = C_4H_3(C_2H_5)NH + C_2H_4O_2$. It boils at 165°. When heated with acetic anhydride, it becomes *n*-acetyl-ethyl pyrrol, $C_4H_3(C_2H_5)N.CO.CH_3$, and ethylpyrrol methyl ketone,  $C_4H_2(NH)\langle\begin{smallmatrix}C_2H_5\\CO.CH_3\end{smallmatrix}$ (*Berichte*, **19**, 2189).

Trimethyl Pyrrol, $C_4H(CH_3)_3NH$. The two possible isomerides appear to be contained in that portion of the bone oil that boils at 180–195° (*Berichte*, **14**, 1342).

β-**Isopropyl Pyrrol**, $C_4H_3(C_3H_7)NH$, is formed, analogous to ethyl pyrrol, by the action of zinc chloride upon a mixture of pyrrol and acetone. It is an oil, boiling at 175°. It forms *β*-pyrrolcarboxylic acid when fused with caustic alkali (*Berichte*, **20**, 855).

aa-**Methyl Phenyl Pyrrol**,  $C_4H_2(NH)\langle\begin{smallmatrix}CH_3\\C_6H_5\end{smallmatrix}$, is formed by heating acetophenone-acetone, $C_6H_5.CO.CH_2.CH_2.CO.CH_3$, with alcoholic ammonia (p. 542). It crystallizes in brilliant white leaflets, that turn red on exposure, melt at 101°, and sublime with partial decomposition.

aa-**Diphenyl Pyrrol**,  $C_4H_2(NH)\langle\begin{smallmatrix}C_6H_5\\C_6H_5\end{smallmatrix}$ (1, 4), is produced by the distillation of pyrrol dibenzoic acid (p. 549), and from *aa*-diphenyl-pyrrol carboxylic acid (p. 548). It melts at 143.5° (*Berichte*, **21**, 3061).

Tetraphenyl Pyrrol, $C_4(NH)(C_6H_5)_4$, from bidesyl, melts at 211° (*Berichte*, **22**, 553).

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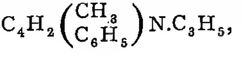
a-Dimethyl pyrrols, in which the imide-hydrogen is also replaced by alkyls, are formed by the elimination of carbon dioxide from their dicarboxylic acids (obtained from diacetosuccinic ester and the primary amines, p. 546) (*Annalen*, **236**, 303).

aa-**Dimethyl-*n*-methyl Pyrrol**, $C_4H_2(CH_3)_2.N,CH_3$, Trimethyl Pyrrol, boils at 169°. *aa*-**Dimethyl-*n*-phenyl pyrrol**, $C_4H_2(CH_3)_2N.C_6H_5$, is solid, melts at 52°, and boils at 252° (Corr.). *aa*-**Dimethyl *a*-naphthyl pyrrol**, $C_4H_2(CH_3)_2N.C_{10}H_7$, melts at 71° and boils at 341° (Corr.).

a-Methyl-phenyl pyrrols, the imide-hydrogen of which has also been replaced by alkyls, are produced from their monocarboxylic acids (obtained from acetophenone-aceto-acetic ester and amines) (p. 546) by the loss of carbon dioxide (*Berichte*, **18**, 2595).

aa-**Methyl-phenyl-*n*-allyl-pyrrol**,  $C_4H_2\left(\begin{smallmatrix}CH_3\\C_6H_5\end{smallmatrix}\right)N.C_3H_5$, melts at 52° and boils at 278°.

aa-Methylphenyl-*n*-phenyl pyrrol, $C_4H_2\left(\begin{matrix}CH_3\\C_6H_5\end{matrix}\right)N.C_6H_5$, melts at 84°.

Pyrrol derivatives, whose imide-hydrogen is replaced by divalent radicals, are produced in an analogous manner by the action of the diamines (*e.g.*, ethylene diamines, phenylenediamine, benzidine) upon acetonyl acetone, as well as upon acetophenone-aceto-acetic ester. The compound, $C_4H_2(CH_3)_2:N.CH_2.CH_2.N:C_4H_2(CH_3)_2$, is thus formed from ethylene diamine and acetonyl acetone (*Berichte*, 19, 3157). Other amide compounds, such as the amido-phenols and the amido-acids, react similarly with acetonyl acetone and acetophenone-aceto-acetic ester, forming complex pyrrol imides (*Berichte*, 19, 558 and 3158).

PYRROL AZO-COMPOUNDS.

The *azo-* and *disazo*-derivatives of pyrrol are analogous to the benzene azo- dyestuffs. They result from the action of the salts of the benzene diazo-compounds upon pyrrol, the pyrrol homologues, and the *n*-alkyl pyrrols, $C_4H_4N.R$, by the entrance of one and two molecules of the diazo-compounds :—

$$\underset{\text{Pyrrol-azo-benzene.}}{C_4H_3(NH).N{:}N.C_6H_5} \quad \text{and} \quad \underset{\text{Pyrrol-disazo-benzene.}}{C_4H_2(NH)\begin{matrix}\diagup N{:}N.C_6H_5\\ \diagdown N{:}N.C_6H_5\end{matrix}}.$$

The mono-azo-compounds are formed in acid solutions, and the disazo-derivatives in neutral or alkaline solution. The former dissolve in concentrated sulphuric acid with a yellow color, the latter with a dark blue coloration (*Berichte*, 19, 2251).

PYRROL KETONES. PSEUDO-ACETYL PYRROLS.

The pyrrol-methyl ketones, or *c*-acetyl pyrrols (together with the isomeric *n*-acetyl pyrrols, p. 540), are produced by heating the pyrrols with acetic anhydride, and are also prepared by a *molecular* rearrangement of the *n*-acetyl pyrrols on being heated to 250° (*Berichte*, 18, 1828):—

$$C_4H_4N.CO.CH_3, \qquad \text{yields} \qquad C_4H_3(NH).CO.CH_3.$$

The acetyl group is linked to carbon. They are distinguished from the *n*-acetyl pyrrols by the fact that when they are boiled with caustic potash they are not decomposed. Being ketones they unite with hydroxylamine and phenylhydrazine. They condense with benzaldehyde, when acted upon with caustic potash, to cinnamyl-pyrrols. The latter serve to characterize the alkyl pyrrols (*Berichte*, 22, 1918).

a-**Pyrryl-methyl Ketone**, $C_4H_3(CO.CH_3)NH$, pseudo-acetyl pyrrol, resulting from pyrrol and acetic anhydride (*Berichte*, 16, 2348), crystallizes from hot water in long needles, that melt at 90°, and boil about 220°. It is volatile in steam. It forms an acetoxime, $C_4H_3\left(C\begin{matrix}\diagup\!\!\diagup N.OH\\ \diagdown CH_3\end{matrix}\right)NH$, with hydroxylamine, which melts at 146°. Potassium permanganate oxidizes it to the ketonic acid, $C_4H_3(NH).CO.CO_2H$ (p. 548). Sodium amalgam converts it into pyrryl-methyl carbinol, $C_4H_3(NH).CH(OH).CH_3$, and pyrryl-methyl pinacone (*Berichte*, 19, 2204).

When bromine acts upon pyrryl-methyl ketone in glacial acetic acid it converts it into bromine substitution products. If added to cold, fuming nitric acid dinitropyrrol (p. 541), one dinitro and two mono-nitro- products of pyrryl-methyl ketone are formed (*Berichte*, 19, 1078).

Pyrryl-ethyl Ketone, $C_4H_3(CO.C_2H_5)NH$, Propionyl Pyrrol, resulting from pyrrol and propionic anhydride (together with *n*-propionyl pyrrol, $C_4H_4N.CO.C_2H_5$), melts at 52°, and distils about 225° (*Berichte*, 20, 1761).

Pyrryl Phenyl Ketone, $C_4H_3(CO.C_6H_5)NH$, Benzoyl Pyrrol, is obtained from pyrrol upon heating it with benzoic aldehyde. It melts at 78°.

The diketone is produced upon heating pyrryl-methyl ketone with acetic anhydride to 250°.

Pyrrylene-dimethyl-diketone, $C_4H_2(CO.CH_3)_2NH$, diacetyl pyrrol, crystallizes from hot water in minute needles, melting at 162°. Potassium permanganate oxidizes it to carbopyrryl glyoxylic acid (p. 548) (*Berichte*, 19, 1957).

Dipyrryl Ketone, $CO(C_4H_3.NH)_2$, is produced together with carbonyl pyrrol (p. 540) by the action of phosgene upon potassium-pyrrol, and by the molecular rearrangement of carbonyl pyrrol when the latter is heated to 250°. It melts at 100°, but is not decomposed when boiled with caustic potash. Carbonyl pyrrol also yields **Pyrroyl-pyrrol,** $C_4H_4N.CO.C_4H_3NH$, melting at 63° (*Berichte*, 18, 1828).

PYRROL CARBOXYLIC ACIDS.

The acids derived from pyrrol are perfectly analogous to the aromatic acids. Their manner of formation is very similar to that by which the oxybenzoic acids are produced. They result by the oxidation of the homologous pyrrols when fused with caustic potash:—

$$C_4H_3(NH).CH_3 \quad \text{yields} \quad C_4H_3(NH).CO_2H,$$

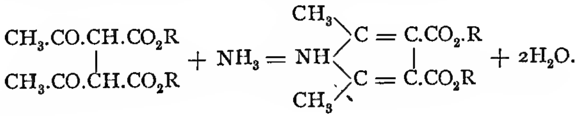
by the action of carbon dioxide upon the potassium derivatives of the pyrrols:—

$$C_4H_4NK + CO_2 = C_4H_3(NH).CO_2K,$$

or by heating the pyrrols with ammonium carbonate, and the action of carbon tetrachloride and alcoholic potash upon pyrrol (*Berichte*, 17, 1439):—

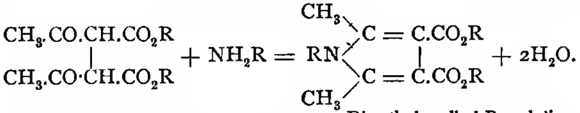
$$C_4H_4NH + CCl_4 + 4KOH = C_4H_3(NH).CO_2H + 4KCl + 2H_2O.$$

Dimethyl pyrrol dicarboxylic acid is prepared in a purely synthetic manner by the action of ammonia upon diaceto-succinic ester (p. 437):—



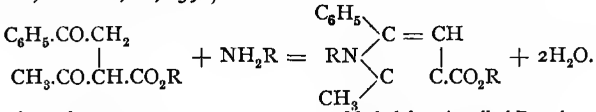
$$\begin{array}{l} CH_3.CO.CH.CO_2R \\ \qquad\qquad | \\ CH_3.CO.CH.CO_2R \end{array} + NH_3 = NH\begin{array}{l} \diagup C(CH_3) = C.CO_2.R \\ \qquad\qquad\qquad | \\ \diagdown C(CH_3) = C.CO_2R \end{array} + 2H_2O.$$

The primary amines react the same as ammonia, with formation of dicarboxylic acids with the alkyl group attached to nitrogen (Knorr, *Berichte*, 18, 299, 1558):—



α-Dimethyl-*n*-alkyl Pyrrol-dicarboxylic Acid.

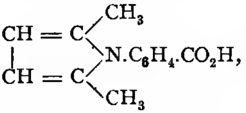
Mono-carboxylic acids of methyl-phenyl pyrrol are also formed from acetophenone- (phenacyl-) aceto-acetic ester, by the action of ammonia and primary amines (Paal, *Berichte*, 18, 2591):—



Acetophenone-aceto-acetic Ester.

α-Methylphenyl-*n*-alkyl Pyrrol-carboxylic Acid.

The action of amido-acids (like glycocoll) upon acetonyl-acetone (p. 328) and acetophenone-aceto-acetic esters produces pyrrol acids, in which the acid residues are combined with nitrogen (Paal, *Berichte*, 19, 559, 3157), *e. g.*,



Dimethyl-pyrrol-benzoic Acid.

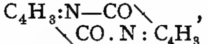
Analogous compounds are also obtained from diaceto-succinic ester (*Annalen*, 236, 314; *Berichte*, 22, 3086).

When the mono- and dicarboxylic acids are heated they part with one and two molecules of carbon dioxide, forming at the same time the corresponding *c*-alkyl pyrrols. When the primary esters of the dicarboxylic acids split off carbon dioxide they pass into the esters of the mono-carboxylic acids.

α-**Pyrrol Carboxylic Acid,** $C_4H_3(NH).CO_2H$, **Carbopyrrolic Acid,** was first obtained from its amide, which is produced together with pyrrol upon distilling ammonium mucate. It is formed (together with β-pyrrol carboxylic acid) when carbon dioxide acts upon potassium-pyrrol heated to 200°, and from pyrrol by heating it with CCl_4 and alcoholic potash, as well as by oxidizing methyl-pyrrol by fusing it with caustic potash. The best method for its preparation consists in heating pyrrol and aqueous ammonium carbonate to 120–130° (*Berichte*, 17, 1150). It crystallizes from water in colorless leaflets or prisms. When these are dry they become green in color. They melt at 192° in a closed tube, decomposing at the same time into carbon dioxide and pyrrol.

Lead acetate does not precipitate its aqueous solution. When digested with dilute acids it breaks up into carbon dioxide and pyrrol red.

The *esters* of the acid are obtained by the action of the alkyl iodides upon its silver salt. The *methyl ester*, $C_4H_3(NH).CO_2.CH_3$, melts at 73°; the *ethyl ester* at 39°. The *amide*, $C_4H_3(NH).CO.NH_2$, is formed together with pyrrol by the distillation of ammonium pyromucate. It consists of shining leaflets, melting at 176.5°. It is decomposed into ammonia and carbopyrrolic acid when boiled with baryta water.

Pyrocoll, $C_{10}H_6N_2O_2 =$  $C_4H_3{:}N\genfrac{}{}{0pt}{}{-CO\diagdown}{\diagdown CO.N:C_4H_3}$, the amide anhydride of carbopyrrolic acid, is produced in the distillation of gelatine (p. 539) and is artificially prepared by heating carbopyrrolic acid with acetic anhydride. It crystallizes in yellow leaflets, melting about 268°. It yields α-carbopyrrolic acid when it is boiled with potash. Its formula is established by a molecular weight determination by Raoult's method (*Berichte*, 22, 2501). Bromine converts it into mono-, di- and tetrabrompyrocoll. These yield brominated pyrrol carboxylic acids when boiled with alkalies. When it is heated with PCl_5, *perchlorpyrocoll*, $C_{10}Cl_6N_2O_2$, and the *octochloride*, $C_{10}Cl_6(Cl_8)N_2O_2$, are produced. Zinc and acetic acid convert the latter into perchlorpyrrol, C_4Cl_4NH, and on boiling with dilute acetic acid we obtain the imide of dichlormaleïc acid (p. 428).

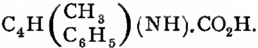
When pyrocoll is dissolved in nitric acid dinitropyrocoll results; sodium hydroxide converts this into nitrocarbopyrrolic acid. The latter crystallizes from water in needles, melting at 146°. The nitration of α-carbopyrrolic acid produces dinitropyrrol (*Berichte*, 19, 1079); the methyl ester cannot be directly nitrated (*Berichte*, 22, 2503).

β-Pyrrol Carboxylic Acid, $C_4H_3(NH).CO_2H$ (2 – 3), is produced on fusing β-methyl pyrrol with KOH, and by the action of CO_2 upon potassium-pyrrol at 200°. From an aqueous solution of the two acids, lead acetate only precipitates the β-acid. It crystallizes in needles, melting at 161–162° with decomposition into carbon dioxide and pyrrol. The same decomposition occurs when its aqueous solution is evaporated.

Methyl Pyrrol Carboxylic Acids, $C_4H_2(CH_3)(NH).CO_2H$. Two of the six isomerides are known. They are produced when carbon dioxide acts upon the potassium derivative of the crude methyl pyrrol (α and β). The lead salt of the β-acid is very insoluble. The α-acid crystallizes from water in small leaflets. It melts at 169°; the β-acid melts at 142°. Both acids, when heated beyond their melting points, decompose into carbon dioxide and the corresponding methyl pyrrols. This occurs with the β-acid on evaporating its aqueous solution.

(1, 4)-Dimethyl Pyrrol-β-Carboxylic Acid, $C_4H\,(CH_3)_2(NH).CO_2H$. Its methyl ester is obtained by distilling the monoethyl ester of α-dimethylpyrrol dicarboxylic acid, when it loses carbon dioxide. It melts at 118°. The free acid consists of needles, melting at 210–213°, and then decomposes into carbon dioxide and $\alpha\alpha$-dimethyl pyrrol. This happens also when it is treated with concentrated acids.

Two isomeric (1, 3)-dimethyl pyrrol-carboxylic acids, $C_4H(CH_3)_2(NH).CO_2H$, from (1, 3)-dimethyl-pyrrol-dicarboxylic acid (p. 549) and tetramethylpyrocoll, melt at 183° and 137° respectively (*Berichte*, 22, 40).



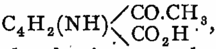
(1,4)-Methyl-phenyl-pyrrol-β-carboxylic Acid, $C_4H\left(\begin{matrix}CH_3\\C_6H_5\end{matrix}\right)(NH).CO_2H$. Its ethyl ester is produced by the action of ammonia upon acetophenone-acetoacetic ester (p. 546). The free acid crystallizes from glacial acetic acid in yellow needles, decomposes partially at 175°, and melts about 190°.

Its derivatives, containing alkyl or phenyl groups attached to the N-atom, are similarly produced by the action of primary amines upon acetophenone-acetoacetic ester (p. 546).

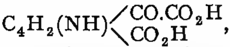
(1, 4)-Diphenylpyrrol-β-carboxylic Acid, $C_4H(C_6H_5)_2(NH).CO_2H$, from acetophenone-benzoyl acetic ester and ammonia (p. 495), melts at 261° (*Berichte*, 21, 3060).

KETONIC ACIDS.

α-Pyrroyl Carboxylic Acid, $C_4H_3(NH).CO.CO_2H$, **Pyrryl Glyoxylic Acid,** is produced by the oxidation of α-pyrryl methyl ketone (p. 544) with alkaline potassium permanganate (*Berichte*, 17, 2949). It crystallizes from water in yellow needles, melting with decomposition at 74–76°. They become anhydrous when placed over sulphuric acid. The anhydrous acid, from benzene, consists of yellow needles, decomposing about 114°. Ferric chloride imparts an intense red color to the aqueous solution. When fused with caustic potash, it becomes α-pyrrol-carboxylic acid (*Berichte*, 19, 1957).

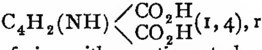


Pyrryl-methyl-ketone Carboxylic Acid, $C_4H_2(NH)\begin{matrix}\diagup CO.CH_3\\\diagdown CO_2H\end{matrix}$, Acetopyrrol carboxylic acid. Its methyl ester is produced on heating α-pyrrol carboxylic methyl ester with acetic anhydride to 250°. It melts at 113°. The free acid is oxidized to carbopyrryl-glyoxylic acid by potassium permanganate (*Berichte*, 19, 1961).

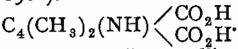


Carbopyrryl Glyoxylic Acid, $C_4H_2(NH)\begin{matrix}\diagup CO.CO_2H\\\diagdown CO_2H\end{matrix}$, is obtained by oxidizing pyrrylene dimethyl diketone (p. 545) with potassium permanganate. It is very unstable. Its *dimethyl ester* melts at 145°. If oxidized by fusion with caustic potash, it yields a pyrrol dicarboxylic acid (*Berichte*, 19, 1959).

DICARBOXYLIC ACIDS.



α-Pyrrol Dicarboxylic Acid, $C_4H_2(NH)\begin{matrix}\diagup CO_2H\\\diagdown CO_2H\end{matrix}(1,4)$, results upon oxidizing carbopyrryl glyoxylic acid by fusion with caustic potash. It separates from alcohol in warty crystals. It turns black when heated to 200°, and breaks up into carbon dioxide and pyrrol. Its *silver salt*, $C_6H_3NO_4Ag_2$, is a caseous precipitate. Its *dimethyl ester*, $C_6H_3NO_4(CH_3)_2$, from the silver salt and ethyl iodide, melts at 132°. The *diethyl ester* melts at 82° (*Berichte*, 19, 1960).



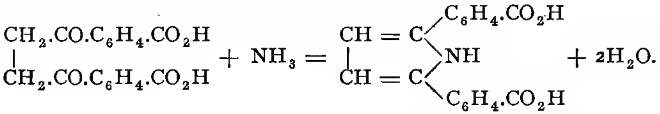
(1,4)-Dimethyl pyrrol-(2,3)-dicarboxylic Acid, $C_4(CH_3)_2(NH)\begin{matrix}\diagup CO_2H\\\diagdown CO_2H\end{matrix}$. Its ethyl ester is derived from diaceto-succinic ester and ammonia. It crystallizes in minute needles, and melts at 99°. If the diethyl ester be saponified with alcoholic potash the *ester acid*, melting at 227°, and the free dicarboxylic acid result. The mineral acids precipitate the latter from its salt solutions in minute needles. It crystallizes from alcohol in long needles. It melts at 251°, and decomposes readily into two molecules of carbon dioxide and (1,4)-dimethyl pyrrol. It sustains the same decomposition when it is boiled with water, or is acted up with concentrated acids (*Berichte*, 18, 1558).

For those derivatives of dimethyl pyrrol-dicarboxylic acid, in which the alkyls and acid residues are attached to the nitrogen atom, consult *Annalen*, 236, 303. Hydroxylamine and phenylhydrazine convert diaceto-succinic ester (*Annalen*, 236, 294) into—

$$C_4(CH_3)_2(N.OH)(CO_2R)_2 \text{ and } C_4(CH_3)_2(N.NH.C_6H_5)(CO_2R)_2.$$

Unsymmetrical (1, 3)-Dimethylpyrrol Dicarboxylic Acid, $C_4(CH_3)_2(NH)\left\langle\begin{matrix}CO_2H\\CO_2H\end{matrix}\right.$. Its diethyl ester may be prepared by reducing a mixture of acetoacetic ester and nitroso-acetic ester with zinc dust in an acetic acid solution (*Annalen*, 236, 217). It melts at 135°, and also forms a potassium salt, $C_{12}H_{16}KNO_4$. If the diethyl ester be saponified two isomeric ester acids (melting at 202° and 197°) and the free dicarboxylic acid result. The latter dissolves quite readily in water, and melts at 197°, decomposing into carbon dioxide and $\alpha\beta'$-dimethylpyrrol (p. 543). It forms an imide anhydride with acetic anhydride (*Berichte*, 21, 2875).

Pyrrol Dibenzoic Acid, $C_4H_2(NH)\left\langle\begin{matrix}C_6H_4.CO_2H\\C_6H_4.CO_2H\end{matrix}\right.$, results from the action of ammonia upon ethylene dibenzoyl-carboxylic acid :—

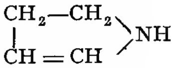


It breaks down into two molecules of carbon dioxide and $\alpha\alpha$-diphenyl pyrrol when distilled with lime (p. 543) (*Berichte*, 20, 1487).

Pyrrylen-phthalide, $C_6H_4\left\langle\begin{matrix}C(N.C_4H_3)\\CO\end{matrix}\right\rangle O$, a derivative of phthalide (see this) is produced, when phthalic anhydride and pyrrol are heated together (*Berichte*, 19, 2201).

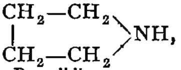
PYRROL HYDRIDES.

Dihydro-Pyrrol or Pyrroline, C_4H_6NH, and Tetrahydropyrrol or Pyrrolidine, C_4H_8NH :—



Pyrroline.

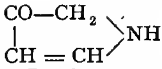
and



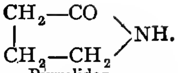
Pyrrolidine.

are formed when hydrogen is added to pyrrol. These are two parent substances from which a series of derivatives can be obtained by the replacement of their hydrogen atoms. Pyrrolidine is perfectly analogous to piperidine.

The following hypothetical parent-nuclei are *keto-derivatives* of pyrroline and pyrrolidine :—


β-Pyrrolon.

and


α-Pyrrolidon.

Pyrroline, C_4H_6NH, is formed when pyrrol is digested with zinc dust and acetic acid. It is a liquid that dissolves readily in water, and boils at 91°. It has an alkaline reaction, smells like ammonia and unites with acids to form salts. It is a secondary base. Nitrous acid converts it into *nitrosamine*, $C_4H_8N(NO)$, melting at 38°.

Pyrrol and methyl iodide unite to dimethyl-ammonium iodide, $C_4H_6N(CH_3)_2I$. Silver oxide converts this into the ammonium hydroxide, $C_4H_6N(CH_3)_2.OH$.

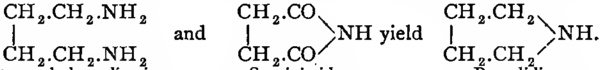
n-**Methyl Pyrroline**, $C_4H_6N.CH_3$, is formed by the action of zinc dust and acetic acid upon *n*-methyl pyrrol. It is very similar to pyrroline and boils at 80°. It unites with methyl iodide to form a dimethyl iodide.

Consult *Berichte*, 22, 2514 upon benzoyl pyrroline, $C_4H_6N.CO.C_6H_5$, and benzyl pyrroline.

The supposed derivatives of β-pyrrolon have been proved to be cyanethyl compounds (*Berichte*, 22, Ref. 325).

PYRROLIDINE COMPOUNDS.

Pyrrolidine, C_4H_8NH, **Tetramethylene-imine**, was first obtained by heating pyrroline with hydriodic acid and phosphorus to 250° (*Berichte*, 18, 2079). It has been synthetically prepared by distilling the hydrochloride of tetramethylene-diamine, and by the action of sodium upon an alcoholic solution of succinimide (*Berichte*, 20, 2215):—


Tetramethylene-diamine. Succinimide. Pyrrolidine.

Pyrrolidine is an alkaline liquid with an odor resembling that of piperidine. It boils at 87°; its sp. gr. at 0° is 0.879. Its *nitrosamine*, $C_4H_8N(NO)$, is a yellow oil boiling at 214° (*Berichte*, 21, 290). It combines with methyl iodide to form HI-methyl-pyrrolidine, $C_4H_8N.CH_3$. This can also be prepared by reducing *n*-methyl pyrroline with hydriodic acid. Methyl pyrrolidine unites with methyl iodide to dimethyl ammonium iodide, $C_4H_8N(CH_3)_2I$, which in its entire behavior resembles piperidine dimethyl iodide, $C_5H_{10}N(CH_3)_2I$. When fused with potassium hydroxide it forms dimethyl pyrrolidine, $C_4H_7N(CH_3)_2$; this yields the ammonium iodide, $C_4H_7N(CH_3)_3I$, with methyl iodide. If this be fused with caustic potash it becomes trimethylamine, $N(CH_3)_3$, and the hydrocarbon C_4H_6 (Pyrrolylen) (*Berichte*, 18, 2081).

α-**Methyl Pyrrolidine**, $C_4H_7(CH_3)NH$, has been prepared by reducing α-methyl pyrrolidon (see below) with metallic sodium and alcohol. It is a strongly alkaline liquid, with a stupefying odor. It boils at 97° (*Berichte*, 22, 1866).

β-**Methyl Pyrrolidine**, $C_4H_7(CH_3)NH$, results from heating β-methyl tetramethylene-diamine (p. 313) hydrochloride. It is a fuming, alkaline liquid, with an odor resembling that of piperidine. It boils at 104° and yields a nitrosamine, boiling at 224° (*Berichte*, 20, 1657).

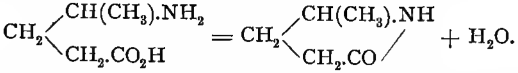
aa-**Dimethyl Pyrrolidine**, $C_4H_8(CH_3)_2NH$, is derived from diamido-hexane (p. 314), and boils at 107° (*Berichte*, 22, 1859; 23, 1544).

Trimethyl Pyrrolidine, $C_4H_5(CH_3)_3NH$, is obtained from amido-trimethyl-butylactinic acid (from diacetonamine (p. 208, with CNH, etc). See *Annalen*, 232, 206.

The following is a keto-derivate of pyrrolidine, C_4H_8NH:—

α-Pyrrolidon, $C_4H_6O(NH)$ (p. 550), is produced when γ-amidobutyric acid is heated to 200° (pp. 369, 372). It distils at 245°. It is a colorless oil, which solidifies upon cooling, and melts at 25–28° (*Berichte*, 22, 3338).

α-Methyl Pyrrolidon, $C_4H_5(CH_3)O(NH)$, is similarly produced upon heating γ-amidovaleric acid to 250° (p. 372) (*Berichte*, 22, 1860):—



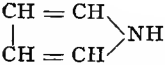
$$\mathrm{CH_2}\left\langle\begin{matrix}\mathrm{CH(CH_3).NH_2}\\ \mathrm{CH_2.CO_2H}\end{matrix}\right. = \mathrm{CH_2}\left\langle\begin{matrix}\mathrm{CH(CH_3).NH}\\ \mathrm{CH_2.CO}\end{matrix}\right\rangle + \mathrm{H_2O}.$$

It forms deliquescent needles, melting at 37°. Nitrous acid converts it into a nitrosamine. Boiling alkalies regenerate γ-amidovaleric acid.

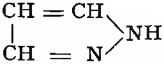
For additional derivatives of pyrrolidon see *Berichte*, 22, 2364; 23, 708, 888.

AZOLE COMPOUNDS.

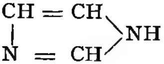
The azoles (diazoles, triazoles, etc.) are those compounds in which there is present a "five-membered" ring, containing two, three, etc., nitrogen atoms. These nuclei can also be derived from pyrrol, by simply replacing the CH-groups by nitrogen. Diazole is known in two isomeric forms—the α- or (1, 2)-*diazole*, and the β- or (1, 3)-*diazole*. The first is also called *Pyrazole*, while the latter is more familiar under the name of *Glyoxaline* or *Imid-Azole**:—



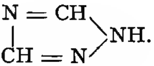
Pyrrol.



α-Diazole, Pyrazole.



β-Diazole, Glyoxaline.



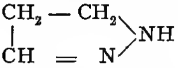
Triazole.

1. PYRAZOLE COMPOUNDS.

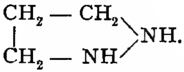
Free **Pyrazole**, $C_3H_4N_2$, is prepared by saponifying the addition product of diazo-acetic ester with acetylene dicarboxylic ester, $C_3HN_2(CO_2.CH_3)_3$ (p. 375), when the three carboxyl groups are split off (*Berichte*, 22, 2165). It can also be obtained from epichlorhydrin by heating it with hydrazine hydrate, $N_2H_4.H_2O$, and zinc chloride (*Berichte*, 23, 1105). It crystallizes in colorless needles, melting at 70° and boiling at 185°. It is feebly basic, reacts neutral, and yields salts that are not very stable.

Only those pyrazole derivatives, containing benzene residues, are known. *Antipyrine* belongs to this class. They will be considered after the aromatic compounds.

The addition of hydrogen to pyrazole produces the basic compounds *Pyrazoline*, $C_3H_6N_2$, and *Pyrazolidine*, $C_3H_8N_2$:—



and



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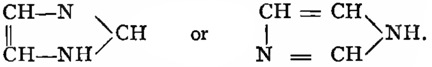
* Consult Widmann, *Jr. pr. Ch.*, 38, 185; *Berichte*, 21, Ref. 888; Knorr, *Berichte*, 22, 2083; Hantzsch, *Annalen*, 249, 4; *Berichte*, 20, 3118.

2. GLYOXALINE COMPOUNDS.

Glyoxaline, $C_3H_4N_2$, the parent substance of the glyoxalines (β-diazoles or imid-azoles) probably possesses the formula :—

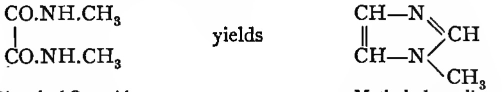


This would ally it both to the amidines, and the anhydrobases and lophines of the benzene series (Japp, *Berichte*, 16, 285, 748).

The glyoxalines, like the amidines, do not yield acidyl derivatives with the acid chlorides, or nitrosamines with nitrous acid. It is for these reasons that the symmetrical formula (without the NH-group) is adopted (Radziszewsky, *Berichte*, 15, 2709) (see below).

Glyoxaline is produced by the action of ammonia upon glyoxal (*Berichte*, 15, 645). It is easily soluble in water, alcohol and ether. It crystallizes in brilliant prisms, melting at 89°, and boiling at 255°. It reacts strongly alkaline, and forms salts with 1 equivalent of the acids. Alkyl iodides and caustic potash cause a substitution of alkyl for the imide hydrogen, forming *n-alkyl glyoxalines* (*Annalen*, 214, 319).

These are liquids with a very peculiar odor. They boil without decomposition, and combine with the alkyl iodides to form ammonium iodides. They can be prepared synthetically by acting upon the dialkyl oxamides with phosphorus pentachloride, and then reducing the amide chlorides and chlorinated bases which form at first. Hence they have been designated *oxalines* (oxalmethylin, oxalethylin) (Wallach, *Annalen*, 214, 257):—



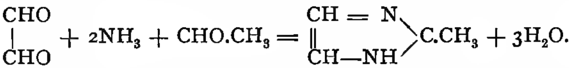
Dimethyl Oxamide. α-Methyl-glyoxaline.

In this manner oxal-ethylin, $C_6H_{10}N_2$, is obtained from diethyl-oxamide. It is identical with *n*-ethyl-*c*-methyl-glyoxaline.

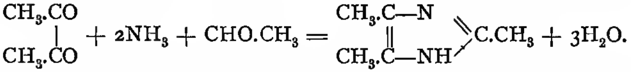
n-Methyl-glyoxaline (*n-Methyl-imid-azole*) has also been made from *n*-methyl-imidazolyl mercaptan (from amido-acetal and methyl mustard oil). This is expressed by the accepted unsymmetrical formula of glyoxaline (imid-azole) (*Berichte*, 22, 1361).

n-Methyl Glyoxaline, $C_3H_3N_2.CH_3$, obtained by the three methods, is a strongly alkaline liquid, boiling at 195–199°. It solidifies in the cold and melts at —5°. *n*-Propyl Glyoxaline, $C_3H_3N_2.C_3H_7$, boils about 221°.

c-Alkyl glyoxalines, homologues of glyoxaline, having the alkyl group attached to carbon, are synthetically produced by the action of ammonia upon a mixture of glyoxal and aldehyde (therefore called glyoxalethylins) (*Berichte*, 17, 2402):—



The reaction occurs more readily by using glyoxal and aldehyde ammonia (*Berichte*, 16, 487). The orthodiketones behave in the same manner with glyoxal. Thus, diacetyl and aldehyde yield *c*-trimethyl glyoxaline (*Berichte*, 21, 1415):—

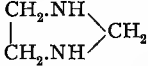


Benzaldehyde and diacetyl also yield dimethyl-phenyl-glyoxaline (*Berichte*, 23, Ref. 248), while triphenyl-glyoxaline (lophine, see this) is produced from benzil (dibenzoyl) and benzaldehyde.

The *c*-alkyl glyoxalines or glyoxalkylins are crystalline solids. They resemble the alkaloids very closely in all their reactions. They are mon-acid imide bases. The imide hydrogen of the latter is replaced by alkyls.

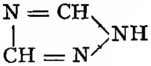
c-**Methyl Glyoxaline**, $C_3H_2(CH_3)N_2H$, glyoxalethylin, consists of brilliant needles, melting at 137°, and boiling at 267°. It is also obtained by a molecular rearrangement of *n*-methyl glyoxaline when the latter is distilled with lime (therefore it is called *Paraoxalmethylin*), and from *c*-methyl-*n*-ethyl glyoxaline, $C_3H_2(CH_3).N_2.C_2H_5$, when this loses ethylene (*Berichte*, 14, 424).

c-**Trimethyl Glyoxaline**, $C_3(CH_3)_3N_2H$, from diacetyl, melts at 183° and boils at 271°.

Derivatives of **Tetrahydroglyoxaline**, $C_3H_8N_2$ =  have been prepared by the action of aldehydes upon ethylene-aniline, $C_2H_4\begin{matrix}\diagup NH.C_6H_5\\ \diagdown NH.C_6H_5\end{matrix}$ (*Berichte*, 20, 732). Hydantoïn may be considered a diketo-derivative of tetrahydroglyoxaline (p. 391).

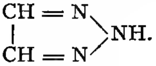
3. TRIAZOLE COMPOUNDS.

The triazole nucleus, of five members, three of which are nitrogen atoms, exists in two isomeric forms:—



Triazole.

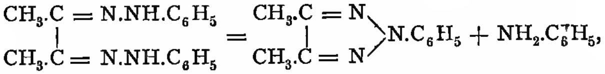
and



Osotriazone.

The **Triazole** derivatives appear to be those compounds, which result from the union of dicyanphenylhydrazine, $C_6H_5.N_2H_3.C_2N_2$, with acid anhydrides, or with benzaldehyde (Bladin, *Berichte*, 19, 2598; 22, 796); ditriazole derivatives (*Berichte*, 22, 3114) are also formed from the so-called cyanphenylhydrazine, $(C_6H_5.N_2H_3)_2C_2N_2$.

The **Osotriazone** derivatives are obtained by boiling the osazones—the dihydrazones of the ortho-diketones (p. 326)—with acids (an amide group is eliminated):—

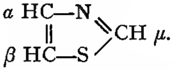


or by the transposition of the osotetrazones which first appear (*Berichte*, 21, 2757). Triphenylosotriazone, $C_3N_3(C_6H_5)_3$ (*Berichte*, 21, 2806) is similarly obtained from benzil dihydrazone.

Urazole is a diketo-derivative of tetrahydrotriazole. Its compounds have been obtained by the action of phenylhydrazine upon urea and derivatives of the latter (*Berichte*, 21, 1219; 20, 3372).

4. THIAZOLE COMPOUNDS.

The thiazole nucleus contains five members; one of them is an N-atom and another an S-atom:—

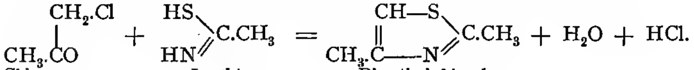


It can be regarded as a diazole, in which the imide group has been replaced by sulphur, or as thiophene in which one CH-group has been substituted by nitrogen. Its entire character is that of pyridine, in which S has replaced *two* CH-groups, without affecting any of the essential properties of the parent substance (just as thiophene is an analogue of benzene) (Hantzsch, *Annalen*, 249, 1; 250, 257; *Berichte*, 20, 3118; 22, Ref. 17 and 256).

Free **Thiazole**, C_3H_3NS, is produced by exchanging hydrogen for the amido group in amidothiazole. This is similar to the formation of benzene from amidobenzene. It is a colorless liquid, boiling at 117°. It resembles pyridine very closely.

The *mono-* and *dialkylic* thiazoles are produced:—

(1) By the condensation of chloracetones with thioacetamides (p. 260):—



Chloracetone. Iso-thio-acetamide. αμ-Dimethyl-thiazole.

Thioacetamide reacts, in a like manner, with chloracetic ester and chlor (brom)-aceto-acetic ester; the products formed first are alkyl thiazole-carboxylic acids, from which the carboxyl groups can be eliminated (*Berichte*, 23, 2341).

(2) By reduction of the oxythiazoles (p. 555) when heating them with zinc dust.

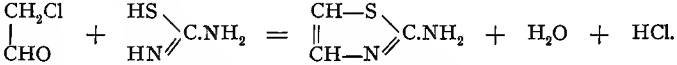
(3) By the transposition of amido-alkylthiazoles, in the same manner as thiazole is obtained from amidothiazole.

The alkylic thiazoles are very similar to their corresponding pyridine bases, and boil usually 2 – 3° higher than the latter. The carboxylic acids of the alkyl thiophenes unite with acids to form salts that are not very stable (*Annalen*, 259, 228, 253, 266).

μ-**Methyl Thiazole**, $C_3H_2(CH_3)NS$, from thiacetamide and chloracetate, boils at 128°. α-**Methyl Thiazole**, from amido-methyl thiazole, and from oxy-methyl thiazole, boils at 132°.

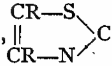
αμ-**Dimethyl Thiazole**, $C_3H(CH_3)_2NS$, from chloracetone and thioacetamide, boils at 145°. It is very similar to lutidine. **Trimethyl–thiazole**, $C_3(CH_3)_3NS$, is obtained from α-chlormethyl aceto-acetic ester (*Berichte*, 23, 2341).

Amidothiazoles result from the condensation of chloraldehyde or chloracetones with thiourea (p. 394):—



Chlor-aldehyde. Isothiourea. μ-Amido-thiazole.

α-Methyl-μ-amidothiazole and α-phenyl-μ-amidothiazole are produced, in a similar manner, from chloracetone and bromacetophenone, $C_6H_5.CO.CH_2Br$.

Alkyl Amido–thiazoles,  are obtained by the action of chloracetones upon mono-alkyl-thioureas, while the dialkyl thioureas yield the **dialkylimido-thiazolines,** 

The amido-thiazoles are very similar to the aromatic amines.

They yield diazo compounds, as well as derivatives of the latter.

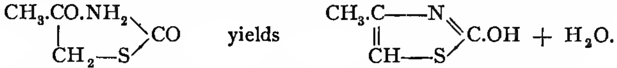
They become thiazoles by replacing the amido-group by hydrogen.

μ-**Amido-thiazole,** $C_3H_2(NH_2)NS$, from chloraldehyde (or dichlor-ester) and thiourea, crystallizes in yellow plates, that melt at 90°. It has an alkaline reaction and forms salts.

α-**Methyl-**μ-**amido-thiazole,** $C_3H(CH_3)(NH_2)NS$, from chloracetone, melts at 42°.

α **Methyl-**μ-**methyl-amidothiazole,** $C_3H(CH_3)NS.NH.CH_3$, from chloracetone and methyl thiourea, is an alkaline oil. It boils at 42° (*Berichte*, **22,** Ref. **21**).

Oxythiazoles are prepared from the sulphocyan-acetones. The carbamine thioacetones formed at first are transposed on boiling with hydrochloric acid:—



Acetone-thiocarbamine. α-Methyl-μ-oxythiazole.

The oxythiazoles are slightly acid, unstable compounds.

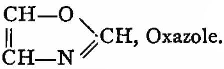
They speedily revert to the carbamin-thio-ketones. They are reduced to thiazoles upon distillation with zinc dust (*Berichte*, **22,** Ref. 18).

Imide-derivatives, compounds of *dihydrothiazole*, or *thiazoline*, C_3H_5NS, are known (*Berichte*, **22,** 1144).

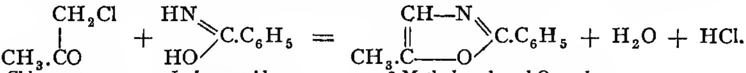
Ethylene-isothiourea, C_3H_5NS (NH), or $C_3H_4NS(NH_2)$, may be viewed as a derivative of thiazoline, C_3H_5NS, or *thiazolidine*, C_3H_7NS (*Berichte*, **23,** 2824).

5. OXAZOLE COMPOUNDS.

The parent nucleus of oxazole is perfectly analogous to thiazole. It contains an oxygen atom instead of the sulphur atom. It bears the same relation to thiazole that furfurane, C_4H_4O, bears to thiophene:—



The alkylic oxazoles, like the alkylic thiazoles, are produced by the condensation of chloracetone with acid-amides (*Berichte*, **21,** 2192):—



Chloracetone. Isobenzamide. β-Methyl-μ-phenyl Oxazole.

The resulting **methyl-phenyl oxazole,** $C_{10}H_9NO$, is a colorless oil, boiling at 240°. It has a feeble, alkaline reaction and dissolves in acids.

Ethylene-pseudo-ureas (p. 391, *Berichte*, **22,** 1151), the products of the transposition of brom-ethyl urea, are derivatives of *dihydro-oxazole*, or *oxazoline*, C_3H_5NO. These are also formed when bromethylamine acts upon acid anhydrides or acid amides (*Berichte*, **22,** 2221; **23,** 2493).

μ-**Methyl-oxazoline,** $C_3H_4ON(CH_3)$, is an oil, with an odor like that of quinoline. It forms salts with acids.

CLASS II.

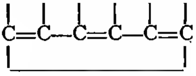
AROMATIC COMPOUNDS OR BENZENE DERIVATIVES.

The aromatic compounds are mostly obtained from aromatic oils and resins. They differ in various respects from the members of the fatty or marsh gas series, but are principally distinguished from the latter by their greater carbon content. The theoretical representations upon their constitution are based chiefly on the views developed by Kekulé in 1865—Kekulé's *benzene theory*. The views of this investigator are in brief as follows (compare Kekulé, *Lehrbuch der org. Chemie; Annalen*, 137, 129):—

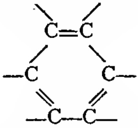
1. All aromatic compounds are derived from a nucleus consisting of six carbon atoms; its simplest compound is *benzene*, C_6H_6. All other aromatic derivatives may be obtained from the latter by substituting other atoms or atomic groups (side chains) for its hydrogen atoms. The new derivatives are distinguished from the methane compounds by their specific benzene character, and are, therefore, called *benzene derivatives*.

2. Benzene has a *symmetrical* constitution. Each carbon atom is combined with one hydrogen atom. Differences between the individual C- and H-atoms have not been discovered. Isomerides are, therefore, only possible when two or more side-chains are present.

3. The structure of the benzene nucleus is such that the six carbon atoms, or CH-groups, form a *closed, ring-shaped* chain, the atoms being joined alternately by single and double bonds:—



or



In benzene, C_6H_6, the fourth affinity of each C-atom is joined to hydrogen; in the benzene derivatives it is combined with other atomic groups.

Derivatives of Benzene.—These may be very readily derived from benzene by the replacement of its hydrogen atoms. Those derivatives in which side-chains exist are easily deprived of these and then revert to benzene.

The closed chain is characterized by great stability, being torn asunder, or dismembered in chemical reactions with great difficulty. This is a property belonging to most all benzene derivatives; it distinguishes the latter from the methane derivatives. In external properties they are better characterized, are more readily crystallized, and are more reactive than the fatty compounds.

The halogens and the nitro- and sulpho-groups can readily replace the hydrogen of benzene:—

C_6H_5Cl	$C_6H_5(NO_2)$	$C_6H_5(SO_3)H.$
$C_6H_4Cl_2$	$C_6H_4(NO_2)_2$	$C_6H_4(SO_3H)_2$
. . .	. . .	. . .

The *union* of the halogen atoms is much firmer in the benzene, than in the methane derivatives; as a general thing they cannot be exchanged for other groups by double decomposition. The production of *nitro-compounds* by the direct action of nitric acid is characteristic of the benzene derivatives, whereas the fatty compounds are generally oxidized and decomposed.

In the reduction of the nitro-derivatives we obtain the *amido-compounds*.—

$C_6H_5.NH_2$	$C_6H_4(NH_2)_2$	$C_6H_3(NH_2)_3$.
Amidobenzene.	Diamidobenzene.	Triamidobenzene.

The so-called azo-derivatives appear as intermediate products of the reaction, whereas when nitrous acid acts on the amido-derivatives the diazo-compounds result. Both classes are of exceptional occurrence in the methane series (p. 167).

Benzene possesses a more negative character than the methane hydrocarbons. The phenyl group, C_6H_5, stands, as it were, between the positive alkyls, C_nH_{2n+1}, and the negative acid radicals. This is evident from the slight basicity of the phenylamines (like $C_6H_5.NH_2$), in comparison with the alkylamines. Diphenylamine, $(C_6H_5)_2NH$, is even a more feeble base, its salts being decomposed by water. Triphenylamine, $(C_6H_5)_3N$, is not capable of yielding salts (*Berichte*, 20, 534).

We discover the same in relation to the hydroxyl derivatives; these, unlike the alcohols, possess a more acid character. The phenols (such as $C_6H_5.OH$, carbolic acid) readily form metallic derivatives with basic hydroxides; trioxy-benzene, $C_6H_3(OH)_3$ (Pyrogallic acid), reacts just like an acid.

By introducing hydroxyl for hydrogen into benzene we obtain the *phenols*, which may be compared to the alcohols:—

$C_6H_5.OH$	$C_6H_4(OH)_2$	$C_6H_3(OH)_3$.
Phenol.	Dioxybenzene.	Trioxybenzene.

These resemble the tertiary alcohols in having the group C.OH attached to the three carbon affinities (p. 118), hence on oxidation they cannot yield corresponding aldehydes, ketones or acids.

The entrance of hydrocarbon groups, C_nH_{2n+1}, into benzene produces the *homologues* of the latter:—

C_6H_6	$C_6H_5.CH_3$	$C_6H_4(CH_3)_2$	$C_6H_3(CH_3)_3$
Benzene.	Methyl Benzene.	Dimethyl Benzene.	Trimethyl Benzene.

$C_6H_5.C_2H_5$	$C_6H_4(C_2H_5)_2$	$C_6H_5.C_3H_7$.
Ethyl Benzene.	Diethyl Benzene.	Propyl Benzene.

Unsaturated hydrocarbons also exist:—

$C_6H_5.CH{=}CH_2$	$C_6H_5C{\equiv}CH$, etc.
Ethenyl Benzene.	Acetenyl Benzene.

In these hydrocarbons the benzene residue preserves the specific properties of benzene; its hydrogen can readily be replaced by halogens and the groups NO_2 and SO_3H. On the other hand, the side-chains behave like the hydrocarbons of the fatty series; their hydrogen can be replaced by halogens, but not by (by action of HNO_3 or H_2SO_4) the groups NO_2 and SO_3H. Different isomeric derivatives are possible, depending upon whether the substitution of the halogens (or other groups) has occurred in the benzene residue or the side-chains, *e. g.*:—

$C_6H_4Cl.CH_3$ and $C_6H_5.CH_2Cl$.
$C_6H_3Cl_2.CH_3$, $C_6H_4Cl.CH_2Cl$ and $C_6H_5.CHCl_2$.

The halogen atoms in the benzene residue are very firmly combined and mostly incapable of double decomposition, while those in the side-chains react exactly as in the methane derivatives.

The substitution of hydroxyl for the hydrogen of the side-chains leads to the true alcohols of the benzene series:—

$C_6H_6.CH_2.OH$
Benzyl Alcohol.

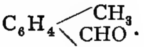
$C_6H_5.CH_2.CH_2.OH$
Phenyl Ethyl Alcohol.


$C_6H_4\begin{array}{l}\diagup CH_3.\\\diagdown CH_2.OH.\end{array}$
Tolyl Alcohol.

The *primary* class is oxidized to *aldehydes* and *acids*:—

$C_6H_5.CHO$
Benzaldehyde.

$C_6H_5.CH_2.CHO$
Phenyl Acetaldehyde.

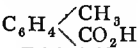

$C_6H_4\begin{array}{l}\diagup CH_3\\\diagdown CHO\end{array}.$
Tolyl Aldehyde.

The acids can be formed by introducing carboxyl groups directly into benzene, or by oxidizing the homologues of the latter:—

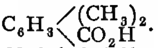
$C_6H_5.CO_2H$
Benzene Carboxylic Acid.

$C_6H_4(CO_2H)_2$
Benzene Dicarboxylic Acid.

$C_6H_3(CO_2H)_3$.
Benzene Tricarboxylic Acid.

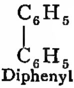

$C_6H_4\begin{array}{l}\diagup CH_3\\\diagdown CO_2H\end{array}$
Toluic Acid.

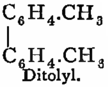
$C_6H_5.CH_2.CO_2H$
Phenyl Acetic Acid.

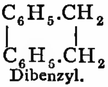

$C_6H_3\begin{array}{l}\diagup (CH_3)_2\\\diagdown CO_2H\end{array}.$
Mesitylenic Acid.

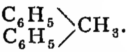
The hydrogen of the benzene residue in these acids, as well as in the alcohols and aldehydes, is replaceable by halogens, and the groups, NO_2, SO_3H, OH, etc.

Furthermore, several benzene residues can unite directly, or through the agency of individual carbon atoms, forming higher hydrocarbons:—


$\begin{array}{l}C_6H_5\\|\\C_6H_5\end{array}$
Diphenyl.


$\begin{array}{l}C_6H_4.CH_3\\|\\C_6H_4.CH_3\end{array}$
Ditolyl.


$\begin{array}{l}C_6H_5.CH_2\\|\qquad\quad|\\C_6H_6.CH_2\end{array}$
Dibenzyl.


$\begin{array}{l}C_6H_5\diagdown\\C_6H_5\diagup\end{array}CH_3.$
Diphenyl Methane.

$C_{10}H_6$
Naphthalene.

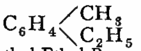
$C_{14}H_{10}$
Anthracene.

$C_{16}H_{12}$.
Chrysene.

Structure of the Isomerides.—Numerous cases of isomerism are possible among the derivatives of benzene. One variety of isomerism corresponds exactly to that observed in the fatty series; it is founded in the isomerism of adjoining groups and their varying union with the benzene residue or in the side-chain. Thus we have the following isomerides of the hydrocarbon, C_9H_{12}:—

$C_6H_5.C_3H_7$ Propyl Benzene.

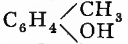
$C_6H_5.C_3H_7$. Isopropyl Benzene.


$C_6H_4\begin{cases}CH_3\\C_2H_5\end{cases}$. Methyl Ethyl Benzene.

$C_6H_3(C_3H_3)_3$. Trimethyl Benzene.

The products obtained by substitution in the benzene residue are isomeric with those derived by the same treatment of the side-chains:—

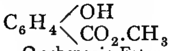
$C_6H_3Cl_2.CH_3$ $C_6H_4Cl.CH_2Cl$ $C_6H_5.CHCl_2$.

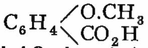

$C_6H_4\begin{cases}CH_3\\OH\end{cases}$ Cresol.

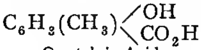
$C_6H_5.CH_2.OH$ Benzyl Alcohol.

$C_6H_5.O.CH_3$. Phenyl Methyl Ether.

The following are also isomeric:—


$C_6H_4\begin{cases}OH\\CO_2.CH_3\end{cases}$ Oxybenzoic Ester.


$C_6H_4\begin{cases}O.CH_3\\CO_2H\end{cases}$ Methyl Oxybenzoic Acid.

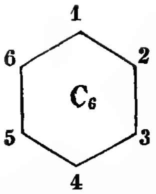

$C_6H_3(CH_3)\begin{cases}OH\\CO_2H\end{cases}$, etc. Oxytoluic Acid.

Another kind of isomerism is based upon the structure of the benzene nucleus, and is conditioned by the relative positions of the substituting groups, hence it is designated *isomerism* of *position* or *place*.

All facts known at present argue with much certainty in favor of the *symmetrical structure* of benzene, that is, that the six hydrogen atoms, or more correctly the six affinities of the benzene nucleus are of *equal value* (same as the four affinities of carbon). Let any one hydrogen atom in benzene be replaced by another atom, or atomic group, and every resulting compound can exist in but one modification; thus there is but *one* chlorbenzene, one nitrobenzene, one amidobenzene, one toluene, one benzoic acid, etc. The following compounds are known in but one modification:—

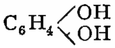
C_6H_5Cl, $C_6H_5(NO_2)$, $C_6H_5.NH_2$, $C_6H_5.CH_3$, $C_6H_5.CO_2H$, etc.

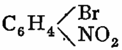
The equal value of the six affinities is indicated not only by the fact that no mono-derivatives, C_6H_5X, can be prepared in more than one modification, but it can be directly proved. Thus in benzene four different hydrogen atoms (1, 2, 3, 4) are replaced by hydroxyl; in each case but one and the same phenol, $C_6H_5.OH$, results (Ladenburg, *Berichte*, 7, 1684). And since two similar ortho- and meta-positions exist in benzene ($2 = 6$ and $3 = 5$, p. 561), the six affinities of the benzene nucleus must be equivalent.

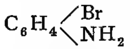


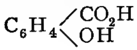
Owing to this symmetry of the benzene nucleus, consisting of six carbon atoms, it can be represented by a regular hexagon; the numbers represent the six affinities, which in benzene compounds are saturated by other atoms or other groups.*

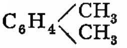
Now, although the six hydrogen atoms in benzene are equal in value, it is obvious from the graphic representation that every di-derivative, $C_6H_4X_2$, can exist in three modifications; their isomerism is dependent upon or due to the relative position of the two substituting groups. Indeed, nearly all di-derivatives are known in *three modifications, but none in more than three.* Thus, there are three dioxybenzenes, three bromnitro-benzenes, three oxybenzoic acids, three toluenes, three dimethyl benzenes, three dicarboxylic acids, etc. The following compounds are known in three modifications each:—

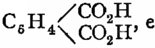

$C_6H_4{<}\begin{matrix}OH\\OH\end{matrix}$


$C_6H_4{<}\begin{matrix}Br\\NO_2\end{matrix}$


$C_6H_4{<}\begin{matrix}Br\\NH_2\end{matrix}$


$C_6H_4{<}\begin{matrix}CO_2H\\OH\end{matrix}$


$C_6H_4{<}\begin{matrix}CH_3\\CH_3\end{matrix}$


$C_6H_4{<}\begin{matrix}CO_2H\\CO_2H\end{matrix}$, etc.

The compounds of the above series can be transformed into each other by various reactions; and, indeed, so that each of the three isomeric modifications (in normal reaction) is transformed into the corresponding modification of the other body. Three isomeric series of di-derivatives of benzene consequently exist; they are designated as the *ortho*, *meta*, and *para* series. We call all those *ortho*-compounds which belong to the series of phthalic acid; the *meta* or *iso-compounds* are those corresponding to isophthalic acid, and *para* those which correspond to parabrombenzoic acid and terephthalic acid.

That an isomeric modification really belongs to one of the three series is determined in a purely empirical manner, either by directly or indirectly converting it into one of the three dicarboxylic acids, $C_6H_4(CO_2H)_2$ (phthalic, isophthalic and terephthalic

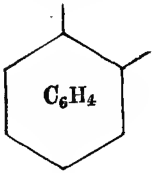
---

* The benzene formula of Kekulé, pictured on p. 556, representing the benzene nucleus, does not fully express the equal value of the six affinities, because according to them the combinations

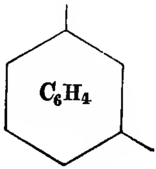
$$\begin{matrix}-CX & & =CX\\ \| & \text{and} & |\\ -CX & & =CX\end{matrix}$$

or the positions (1 : 2) and (1 : 6) are different. According to theory and the formula there are four isomeric di-derivatives, $C_6H_4X_2$, of benzene. But it has been proved that the di-derivatives (1, 2) and (1, 6) are identical, and that only three isomeric di-derivatives are possible (p. 562). The hexagon does not attempt an explanation of the manner in which the fourth affinity of the C-atoms is combined, but it does give full expression to the equal value of the six valences.

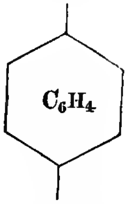
acid). The relative positions of the substituting groups in the benzene nucleus have, however, been ascertained with perfect certainty. In the ortho-compounds two adjoining hydrogen atoms in benzene are replaced (the positions 1 : 2 or 1 : 6; 1 here represents any one of the six similar hydrogen atoms); the meta-compounds have the structure, 1 : 3 or 1 : 5; whereas in the *para*-compounds, two opposite affinities (separated by two carbon atoms) are joined to other atoms (positions 1 : 4). The following graphic representations will better explain the idea under consideration :—



Ortho-derivatives.
(1, 2)



Meta-derivatives.
(1, 3)



Para-derivatives.
(1, 4)

The following substances may be mentioned as chief representatives of the three isomeric series :—

	(1, 2).	(1, 3).	(1, 4).
$C_6H_4\Big\langle\begin{matrix}OH\\OH\end{matrix}$	Pyrocatechin.	Resorcin.	Hydroquinone.
$C_6H_4\Big\langle\begin{matrix}OH\\CO_2H\end{matrix}$	Salicylic Acid.	Oxybenzoic Acid.	Paraoxybenzoic Acid.
$C_6H_4\Big\langle\begin{matrix}CH_3\\CH_3\end{matrix}$	Orthoxylene.	Isoxylene.	Paraxylene.
$C_6H_4\Big\langle\begin{matrix}CO_2H\\CO_2H\end{matrix}$	Phthalic Acid.	Isophthalic Acid.	Terephthalic Acid.

The reasons for supposing that the isomeric di-derivatives possess a structure such as indicated, are;—

(1) Phthalic acid is obtained by the oxidation of naphthalene, and the structure of the latter (see this) is very probably such that the two carboxyl groups in the acid resulting from it can only have the position (1, 2) (Graebe).

(2) The structure of mesitylene, $C_6H_3(CH_3)_3$, is symmetrical; the three methyl groups present in it hold the positions 1, 3, 5 (see p. 566). The formation of mesitylene by the condensation of three molecules of acetone (A. Baeyer) proves this; the substitutions of mesitylene (Ladenburg, *Berichte*, 7, 1133) also indicate it with great certainty. The production of uvitic acid by the condensation of pyroracemic acid (p. 566) argues for the view that in it, and consequently also in mesitylene, the three side groups hold the positions (1, 3, 5). If we replace a CH_2-group in mesitylene by hydrogen, we obtain isoxylene, called dimethyl benzene, $C_6H_4(CH_3)_2$,

in which the two methyl groups can only have the positions (1, 3) = (1, 5). When isoxylene is oxidized, it yields isophthalic acid, $C_6H_5\Big\langle\begin{matrix}CO_2H\\CO_2H\end{matrix}$.

(3) It is apparent, on examining the benzene hexagon, that only a *single position* (4 with reference to 1) is possible for the para-position while two similar positions can exist for the meta- and ortho-derivatives (the positions 3 and 5, and 2 and 6). This can be shown experimentally. It has been proved that the positions 3 and 5 are similar with reference to 1, consequently the meta-derivatives (1, 3) and (1, 5) are identical (*Annalen*, 192, 206, 222, 68). In the same manner the ortho-derivatives (1, 2) and (1, 6) are identical, consequently the positions 2 and 6 are similar (*Berichte*, 2, 141 and *Annalen*, 192, 213)—while the para-position occurs but once in the benzene nucleus (see *Berichte*, 10, 1215). It has been shown that paraoxybenzoic acid, parabromtoluene, and, therefore, also terephthalic occupy it. The latest investigations upon oxy-methyl-ethyl benzonitrile show that the positions 2 and 6 are identical (*Berichte*, 18, Ref. 148), and from the study of bromnitroparatoluidine, it is concluded that this is also the case with the positions 3 and 5 (*Annalen*, 234, 159).

In addition to the preceding we have another means of determining the position, and it leads to exactly the same conclusions (Körner). If we replace another hydrogen atom (by NO_2) in a para compound, (*e. g.*, paradibrombenzene, $C_6H_4Br_2$) it is evident from the figure that but one compound can result, one nitroparadibrombenzene—because the positions 2, 3, 5 and 6 (those which the NO_2 can enter) are alike with reference to the para position 1, 4. But 3 isomeric mononitro derivatives are possible from metadibrombenzene (1, 3); in these the NO_2-group occupies the positions 2, 4 (= 6) or 5. Orthodibrombenzene (1, 2) finally can yield 2 mononitro-derivatives; in these the NO_2-group holds the positions 3 (= 6) and 4 (= 5). Therefore, six isomeric nitrodibrombenzenes, $C_6H_3\Big\langle\begin{matrix}NO_2\\Br_2\end{matrix}$, are possible; 1 derived from the para, 3 from the meta, and 2 from ortho-dibrombenzene; conversely, by the retrogressive substitution of H for NO_2 we discover that paradibrombenzene is afforded by but one nitrodibrombenzene; metadibrombenzene by three other nitrodibrombenzenes, and the ortho-compound by two nitrodibrombenzenes. Körner executed this method of ascertaining position with much satisfaction and certainty with the isomeric tribrombenzenes (*Gazzetta chimica ital.*, 4, 305). The study of the six isomeric nitro- (or amido-) benzoic acids, $C_6H_3\Big\langle\begin{matrix}CO_2H\\(NO_2)_2\end{matrix}$, gave the same results (Griess, *Berichte*, 5, 192 and 7, 1223). Further evidence is derived from the derivatives of the three isomeric xylenes: metaxylene yields three nitroxylenes, three xylidines and three xylenols, the orthoxylene two of each, and the para- but one. From this isoxylene and isophthalic acid must have the positions (1, 3), orthoxylene and phthalic acid (1, 2) and paraxylene and terephthalic acid (1, 4) (*Berichte*, 18, 2687).

That two adjacent carbon atoms of the benzene nucleus carry the side-groups in the *ortho* compounds is further concluded from their ability to yield so-called condensations and various anhydrides (compare the phenylene diamines, thioanilines, coumarines, indols, phthalic acid anhydrides, etc). There are also crystallographic grounds favoring the idea that the meta-compounds stand between those of the ortho and para series (*Zeitschrift f. Kryst.*, 1879, 171).

The benzene hexagon not only expresses all the relations of isomerism of the benzene derivatives, but also abundantly illustrates their chemical and physical deportment.

If three or more hydrogen atoms of benzene be replaced, two cases arise: the substituting groups are like or unlike. In the first instance three isomerides of the tri-derivatives, *e. g.*, $C_6H_3(CH_3)_3$, are possible, and they occupy the positions:—

(1, 2, 3) (1, 2, 4) and (1, 3, 5).

We call them *adjacent* (1, 2, 3) or (*v*) = vicinal, *unsymmetrical* (1, 2, 4) or (*a*) = asymmetrical, and *symmetrical* (1, 3, 5) or (*s*) tri-derivatives.

Three isomeric structural cases exist likewise for the tetra-derivatives, with four similar groups, $C_6H_2X_4$ (analogous to the di-derivatives):—

(1, 2, 3, 4)	(1, 2, 4, 5)	(1, 2, 3, 5).
Adjacent.	Symmetrical.	Unsymmetrical.

Only one modification is possible when there are five and six similar groups; thus there exists but one pentachlorbenzene, C_6HCl_5, and but one hexachloride, C_6Cl_6.

When the substituting groups are unlike, the number of possible isomerides is far greater; they can easily be derived from the hexagon scheme. Thus, six isomeric modifications correspond to the formula of dinitrobenzoic acid, $C_6H_3(NO_2)_2.CO_2H$:—

(1, 2, 3) (1, 2, 4) (1, 2, 5) (1, 2, 6) (1, 3, 4) (1, 3, 5);

here the carboxyl group occupies position 1.

CONSTITUTION OF THE BENZENE NUCLEUS.

In Kekulé's formula the six carbon atoms are attached to each other by alternating single and double bonds, forming a closed ring, consisting of three single and three divalent ethylene linkages (p. 556). These assumptions give a rather comprehensive view of the entire behavior of the benzene derivatives:—

1. They illustrate in the clearest manner possible the methods that have been employed in the synthesis of benzene derivatives (p. 565), benzene condensations, naphthalene, phenanthrene, etc. This has all been verified by the most recent syntheses (that of α-naphthol from phenylisocrotonic acid, etc).

2. They show that only ortho-derivatives (because their side-chains are adjacent) are capable of forming anhydrides, and explain many derivatives due to ortho-condensations. The accepted benzene formula is made quite evident from the manner in which the quinoline ring is formed (Marckwald, *Berichte*, 23, 1015).

3. The assumption of three double unions offers the simplest explanation (without new theories) for the power of benzene derivatives to yield additive products with 2, 4 and 6 affinities (p. 567). True, this addition does not occur as readily with the normal benzene compounds as it does with the methane compounds, in which there exist ethylene unions, but it can be expressed by the ring-formula of the benzene nucleus, and finds analogy in the behavior of the double (divalent) union in phenanthrene (p. 568 and Baeyer, *Annalen*, 251, and 286). Para-additions, it seems, do occur. These are not easily explained. The normal formula only accounts for ortho-additions (p. 568).

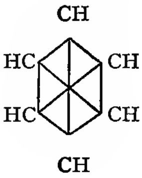
4. Various physical properties argue for the presence of double unions, like those of ethylene, in benzene. Thus, the specific refractive powers indicate the

presence of three ethylene unions, $CH{=}CH$, in benzene compounds, and five in naphthalene (Brühl, *Berichte*, 20, 2288). Compare Nasini, *Berichte*, 23, Ref. 276. The specific volumes of the benzene derivatives appear to support this idea (p. 57 and *Berichte*, 20, 771).

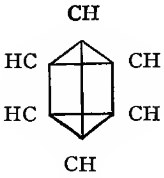
Kekulé's formula for benzene does not fully express the entire symmetry of the benzene nucleus. It would make the ortho-derivatives (1, 2) and (1, 6) different, and allow of four different di-derivatives, unless we admit Kekulé's idea of the oscillations of the adjacent carbon atoms (*Annalen*, 162, 86)

For this and other reasons various benzene formulas have been proposed (see G. Schultz's Chemie des Steinkohlentheers, II Aufl., p. 110), *e. g.*, the *octahedral* formula of Thomsen, the *prism* formula of Ladenburg, and the *diagonal* formula of Claus.

The authors of these three formulas do not regard double unions as present in the normal benzene nucleus, but contend that each carbon atom is united by a single bond to three other carbon atoms. The benzene nucleus, according to this view, contains nine single unions of carbon:—



and



It was thought that this last idea was definitely proved by the specific volumes of the benzene derivatives, and especially by their heat of combustion (Theorie der Bildungswärme von J. Thomsen, *Berichte*, 13, 1808; 14, 2944). According to the most recent researches the specific volumes argue strongly for the presence of three divalent unions in the benzene nucleus, while the conclusions drawn from the heat of combustion are in the opinion of Brühl unfounded (*Journ. prakt. Chemie* (2) Bd., 35, 1).

Ladenburg's *prism* formula fully accounts for all the static relations of benzene, and explains its isomeric derivatives. It, however, ignores all the double unions, which are proved by the partially reduced benzene nuclei of the di- and tetra-hydro-additive products (p. 568). It establishes a spatial orientation of the four affinities of the carbon atoms, which is without analogy in the paraffin series, and, in the opinion of its author, leaves to the formula of Kekulé the first place in explaining the various modes of formation and the decompositions of the benzene compounds (*Berichte*, 23, 1010).

The diagonal formula of A. Claus, with its hexagonal ring and its diagonal or central linkages, explains all the isomeric relations of the derivatives of benzene fully as well as the hexagon formula. It has the advantage that it permits of the formation of either para- or ortho-additive products, because it grants the double carbon-linkages in both the di- and tetra-hydro-benzenes (*Berichte*, 20, 1422; *Journ. pr. Chem.* (2), 42, 458). But it also presents an orientation of the four carbon affinities that is without analogy, and introduces a peculiar central valence, differing from that of the two ring valences.

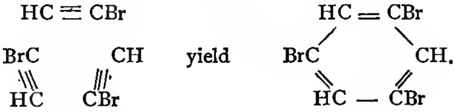
Baeyer has very recently introduced a *central* formula, which is very similar to the diagonal formula, but, unlike the latter, does not admit the presence of central linkages. It does not attempt to account for the state or condition of the fourth valence of carbon, but maintains merely that it exerts a pressure directed towards the centre. It thus reverts to the hexagonal formula of benzene (Kekulé) which makes no attempt to explain the manner in which the fourth valences are combined (Baeyer, *Berichte*, 23, 1775).

Formation of Benzene Derivatives.—The compounds of benzene can only be obtained in exceptional cases from methane derivatives by synthetic reactions. As they are generally very stable on exposure to heat (especially the hydrocarbons and anilines), they are quite often produced by the application of a red heat to the methane derivatives. Thus, benzene and other hydrocarbons result by exposing acetylene to a red heat:—

$$3C_2H_2 = \underset{\text{Benzene.}}{C_6H_6}; \qquad 4C_2H_2 = \underset{\text{Styrolene.}}{C_8H_8}.$$

1. Liquid bromacetylene is readily *polymerized*, when exposed to light, to solid symmetrical tribrombenzene (*Berichte*, **18**, Ref. 374):—

$$3C_2HBr = C_6H_3Br_3 \ (1, 3, 5) \text{ or}$$



When iodo-acetylene, C_2HI, is preserved for some time it also becomes tri-iodobenzene, $C_6H_3I_3$. When di-iodoacetylene, C_2I_2, is exposed to light or heat, it forms hexa-iodo-benzene, C_6I_6 (*Berichte*, **18**, 2276).

Symmetrical trimethyl benzene (mesitylene) is similarly obtained from allylene, $CH_3.C:CH$, on distilling its sulphuric acid solution:—

$$3CH:C.CH_3 = C_6\ H_3(CH_3)_3.$$

The polymerization of crotonylene, $CH_3.C{:}C.CH_3$ (p. 89), occurs even more readily, since shaking it with sulphuric acid suffices for its conversion into hexamethyl benzene, $C_{12}H_{18}$ (*Berichte*, 14, 2073):—

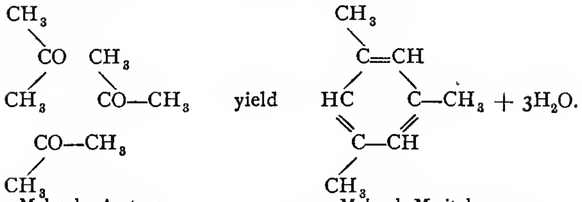
$$3CH_3.C{:}C.CH_3 = C_6(CH_3)_6.$$

The transposition of propiolic acid (p. 244), when exposed to light, into trimesic acid (symmetrical benzene tricarboxylic acid (*Berichte*, 19, 2185) is due to the same polymerization:—

$$3HC{:}C.CO_2H = C_6H_3(CO_2H)_3 \ (1, 3, 5).$$

2. The formation of benzene compounds from ketones (by *hydrolytic condensation*) is very interesting. The condensation here is probably analogous to that of crotonaldehyde from aldehyde (p. 194), and mesityl oxide from acetone (p. 207). Symmetrical trimethyl benzene (mesitylene) is formed rather abundantly on distilling acetone with sulphuric acid:—

$$3CO(CH_3)_2 = C_6H_3(CH_3)_3 + 3H_2O, \text{ or}$$



3 Molecules Acetone. 1 Molecule Mesitylene.

We can obtain in a similar manner symmetrical triethyl benzene, $C_6H_3(C_2H_5)_3$, from methyl-ethyl ketone, $CH_3.CO.C_2H_5$, tripropyl benzene, $C_6H_3(C_3H_7)_3$, from methyl-propyl ketone, $CH_3.CO.C_3H_7$, and triphenyl benzene, $C_6H_3(C_6H_5)_3$, from methyl-phenyl ketone, $CH_3.CO.C_6H_5$.

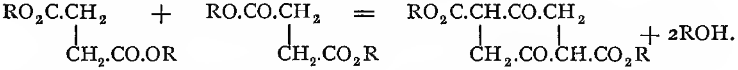
Analogous condensations are the following:—

Formo-acetic ester, $CHO.CH_2.CO_2R$, to trimesic ester, $C_6H_3(CO_2R)_3$; acetaldehyde to symmetrical triacetyl benzene, $C_6H_3(CO.CH_3)_3$ (p. 323); pyroracemic acid to uvitic acid, $C_6H_3.(CH_3).(CO_2H)_2$ (reduction of the carboxyl group to CH_3); aceton-oxalic ester to symmetrical oxytoluic acid, $C_6H_3(CH_3)(OH)CO_2H$ (p. 341).

Another rather remarkable condensation is that of the ortho-diketones to quinogens and quinones (p. 326).

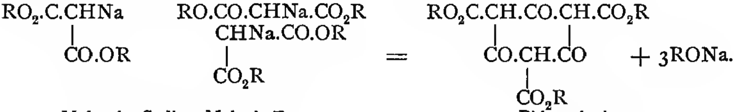
3. Another synthetic method employed in the production of benzene derivatives depends upon condensation, analogous to that observed in the formation of aceto-acetic ester (p. 334). It occurs in the action of sodium upon various acid esters, when sodium ethylate or alcohol is split off, and, therefore, may be termed an *ester condensation.*

Succino-succinic ester (quinone tetrahydro-dicarboxylic ester) (p. 342) is formed by the action of sodium upon ethyl succinic ester:—



$$\begin{array}{l} RO_2C.CH_2 \\ \quad | \\ \quad CH_2.CO.OR \end{array} + \begin{array}{l} RO.CO.CH_2 \\ \quad | \\ \quad CH_2.CO_2R \end{array} = \begin{array}{l} RO_2C.CH.CO.CH_2 \\ \quad\ |\qquad\quad | \\ \quad CH_2.CO.CH.CO_2R \end{array} + 2ROH.$$

Again, upon heating sodium malonic ester phloroglucintricarboxylic ester results (p. 409):—



$$\begin{array}{l} RO_2.C.CHNa \\ \quad | \\ \quad CO.OR \end{array} \quad \begin{array}{l} RO.CO.CHNa.CO_2R \\ \quad CHNa.CO.OR \\ \quad | \\ \quad CO_2R \end{array} = \begin{array}{l} RO_2C.CH.CO.CH.CO_2R \\ \qquad |\qquad\quad | \\ \qquad CO.CH.CO \\ \qquad\quad | \\ \qquad\quad CO_2R \end{array} + 3RONa.$$

3 Molecules Sodium Malonic Ester. Phloroglucin-tricarboxylic Ester.

Similarly, acetone dicarboxylic ester yields, on heating its sodium compound, dioxyphenylaceto-dicarboxylic ester, which can easily be converted into orcinol (*Berichte*, 19, 1446):—

$$2CO\Big\langle\begin{array}{l} CH_2.CO_2R \\ CH_2.CO_2R \end{array} = C_8H_3O_2\left\{\begin{array}{l} CH_2.CO_2R \\ (CO_2R)_2 \end{array}\right. + ROH + H_2O.$$

In this reaction there occurs first an ester, then a ketone condensation.

The ester of trimesic acid is produced when sodium acts upon a mixture of acetic ester and formic ester, water and sodium ethylate splitting off at the same time.

4. When hexyl iodide, $C_6H_{13}I$, and ICl_3 are heated together the two terminal C-atoms unite, and the product is hexachlorbenzene, C_6Cl_6, and when heated with bromine hexabrombenzene results, even at 200° C.

Another interesting synthesis is that of benzene hexacarboxylic acid, $(C_6(CO_2H)_6) = C_{12}H_6O_{12}$, mellitic acid, by the oxidation of graphite or charcoal with potassium permanganate, and that of the potassium derivative of hexaoxybenzene, $C_6(OH)_6$, upon heating CO with potassium (Nietzki, *Berichte*, 18, 1836):—

$$6CO + 6H = C_6O_6H_6.$$

The normal benzene nucleus, formed as above, is very stable. It is broken only when exposed to exceptionally energetic reactions. The following decompositions are effected quite readily, and are, therefore, worthy of mention: the conversion of proto-catechuic acid and pyrocatechol into dioxytartaric acid by nitrous acid; benzene into trichloraceto-acrylic acid and maleïc acid (p. 344) by chloric acid, and gallic acid, salicylic acid and phenol into isotrichlorglyceric acid (p. 461). Chlorine changes phlorglucin quite easily into dichloracetic acid and tetrachloracetone (p. 205), while potassium chlorate and hydrochloric acid decompose chloranilic acid into tetrachloracetone and tetrachlordiacetyl (p. 327).

The intermediate transposition of various chlorine derivatives, by the action of chlorine, into keto-derivatives of pentamethylene is rather peculiar (p. 520).

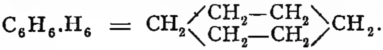
All benzene compounds are decomposed when oxidized by energetic reagents, such as chromic acid, etc.

Additive Products.—Many benzene derivatives are able to combine directly with 2, 4 and 6 atoms of chlorine, bromine, hydrogen, etc. Here the three double bonds of the carbon atoms, as in the ethylenes, in all probability, change to single bonds:—

$$C_6H_6.Cl_2 \quad C_6H_6.Cl_4 \quad C_6H_6.Cl_6.$$

Nascent hydrogen converts the phthalic acids into di-, tetra, and hexa-hydrophthalic acids. The halogens are added with much more difficulty than in the case of the alkylens and other unsaturated fat-bodies, although the latter sometimes take up the halogens with difficulty (see fumaric acid). These addition products contain the ring-shaped, closed benzene chain, and are the compounds, C_6X_{12}, no longer able to saturate additional affinities. When the benzene ring is broken, hexane derivatives, C_6X_{14} result. The addition products are, therefore, true benzene derivatives, and can readily be converted into the normal compounds, C_6X_6 (p. 571). . .

The latest researches of Baeyer prove that hexa hydrobenzene, $C_6H_6.H_6$, is in fact identical with hexamethylene (analogous to tetra- and penta-methylene) (Baeyer, *Annalen*, 245, 131; *Berichte*, 21, Ref. 495):—



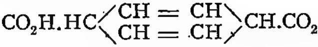
$$C_6H_6.H_6 = CH_2\left\langle\begin{matrix}CH_2-CH_2\\CH_2-CH_2\end{matrix}\right\rangle CH_2.$$

Baeyer designates the normal benzene ring, C_6H_6, in which each C-atom is combined with three affinities to carbon, as the *tertiary* benzene ring, the added ring, C_6H_{12}, as the *secondary* or reduced benzene ring.

The partially reduced rings, $C_6H_6.X_2$ and $C_6H_6.X_4$, contain one and two double-unions, C=C, which behave just like those of the olefines. Like the latter, they are readily oxidized by alkaline permanganate, whereas terephthalic acid is not attacked in the cold by this reagent. It might be deduced from this that an ordinary double-union does not occur in the normal benzene ring; further, that para-compounds also occur, as the additions sometimes take place at the para carbon atoms. Baeyer, however, thinks that these abnormalities are explained by the like deportment of phenanthrene (the non-oxidation of its double-linkage) and by the molecular transpositions of the hydrogen additive products (*Annalen*, 251, 258; 256, 1, *Berichte*, 22, Ref. 375; 23, 231; 23, 1272).

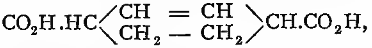
The additions to the ortho-, para, and meta-carbon atoms occur more conveniently if we adopt the diagonal formula of Claus (*Jr. pk. Chem.* 42, 461; *Berichte*, 20, 1424).

Baeyer indicates the double-union in the reduced benzene nuclei, $C_6H_6.X_2$ and $C_6H_6.X_4$, by the character Δ, adding a number as index to show which carbon atom of the hexagon (p. 560) is in double union with the adjacent (next following) carbon atom. Thus, $\Delta^{2,5}$-Dihydro-terephthalic acid represents a para-dicarboxylic acid in which the second C-atom is doubly united with the third C-atom, and the fifth C-atom doubly linked to the sixth C-atom. Δ^{2}-Tetrahydro-terephthalic acid is a substance in which the second carbon atom is doubly linked to the third carbon atom:—



$$CO_2H.HC\left\langle\begin{matrix}CH = CH\\ CH = CH\end{matrix}\right\rangle CH.CO_2H$$

$\Delta^{2,5}$-Dihydroterephthalic acid.



$$CO_2H.HC\left\langle\begin{matrix}CH = CH\\ CH_2 - CH_2\end{matrix}\right\rangle CH.CO_2H$$

Δ^{2}-Tetrahydroterephthalic acid.

A. Baeyer has developed *stereochemical* representations as to the constitution of hexa-hydro-benzene derivatives. These would explain the existence of two isomeric hexa-hydroterephthalic acids, two hexahydromellitic acids, etc. (Baeyer, *Annalen*, 258, 1, 145.) See also Sachse, *Berichte*, 23, 1363 (compare Herrmann, *Berichte*, 23, 2060).

HYDROCARBONS, C_nH_{2n-6}.

The benzene homologues are formed by substituting alkyls in benzene for hydrogen:—

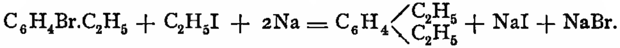
C_6H_6	Benzene.	B. P. 80.5°.
$C_6H_5.CH_3$	Toluene.	110°.
$C_6H_4(CH_3)_2$	Xylenes.	137–140°.
$C_6H_3(CH_3)_3$	Trimethyl Benzenes.	163–170°.
$C_6H_2(CH_3)_4$	Durene.	190°.
$C_6H_5.C_2H_5$	Ethyl Benzene.	134°.
$C_6H_5.C_3H_7$	Propyl Benzene.	157°.
$C_6H_5.C_3H_7$	Isopropyl Benzene.	151°.
$C_6H_5.C_4H_9$.	Isobutyl Benzene.	163°.

The entrance of the methyl group into the benzene nucleus elevates the boiling point about 29–26°; its introduction in the side-chains causes an increase of about 23–19°. The boiling points of isomerides of position (p. 559) usually lie near each other; the ortho-compounds boil about 5°, and the meta- 1° higher than the para-derivatives.

Preparation.—The most important methods of preparing the benzene hydrocarbons are the following:—

(1) Action of sodium upon mixtures of their bromides, and the bromides or the iodides of the alkyls in ethereal solution; reaction of Fittig (p. 72):—

$$C_6H_5Br + CH_3I + 2Na = C_6H_5.CH_3 + NaI + NaBr,$$



$$C_6H_4Br.C_2H_5 + C_2H_5I + 2Na = C_6H_4\Big\langle\begin{matrix}C_2H_5\\C_2H_5\end{matrix} + NaI + NaBr.$$

In carrying out these syntheses mix the bromide with the alkyl iodide and ether (free from water and alcohol), then add metallic sodium in thin pieces and allow to stand for some time, after which the solution is heated with a return condenser upon a water bath. A few drops of acetic ether sometimes accelerates the reaction. Para- and ortho-derivatives, *e. g.*, $C_6H_4Br.CH_3$ and $C_6H_4Br_2$, react most readily. With the meta-compounds, which are not so easily attacked, bromides are substiuted for alkyl iodides, or else benzene iodides are employed. (See *Berichte*, 21, 3185, for the course of the reaction.)

(2) Action of the alkylogens upon benzene hydrocarbons in the presence of aluminium chloride (zinc or ferric chloride)—*Friedel* and *Crafts*.

It is very likely that in this reaction metallo-organic compounds, *e. g.*, $C_6H_5.Al_2Cl_5$, are formed, which afterwards act upon the alkylogens:—

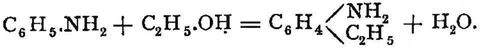
$$C_6H_6 + CH_3Cl = C_6H_5.CH_3 + HCl,$$
$$C_6H_6 + 2CH_3Cl = C_6H_4(CH_3)_2 + 2HCl, \text{ etc.}$$

Even hexamethyl benzene, $C_6(CH_3)_6$, can be prepared after this manner. Various halogen derivatives, *e. g.*, chloroform (see diphenyl methane) and acid chlorides (see ketones) react similarly with the hydrocarbons of the benzene series.

To effect syntheses after this style, $AlCl_3$ ($\frac{1}{5}$–$\frac{1}{3}$ part) is added to benzene, and CH_3Cl or C_2H_5Cl is conducted into the heated mixture; or $AlCl_3$ can be added to the benzene compound mixed with the chloride or bromide, and heat then applied until the evolution of HCl has almost ceased (*Berichte*, 16, 1745). Carbon disulphide sometimes acts very favorably as a diluent. The product is gradually mixed with water, then digested with soda. The oil which separates is subjected to distillation. Consult *Berichte*, 14, 2624, upon the introduction of methyl into homologous benzenes. A table of all the syntheses effected by $AlCl_3$ may be found in *Annalen Chim. Phys.*, (6) I, 449.

Frequently the action of the $AlCl_3$ is much more complicated, inasmuch as syntheses are not the only products, but we also find decompositions, splitting-off and transference of the alkyls. Thus, from toluene we obtain benzene, xylene, etc., (Anschütz, *Berichte*, 18, 338, 657; Friedel, *Berichte*, 18, Ref. 336). A tabulation of the more complex reactions can be found in *Annalen*, 235, 150, 299.

The benzene nucleus may be alkylized if the HCl-salts of alkylic anilines be heated alone, or if the anilines and methyl alcohol be heated to 250–300°; here the NH_2 group is eliminated (*Berichte*, 13, 1729); or the anilines and fatty alcohols can be heated with zinc chloride to 250° (*Berichte*, 16, 105):—



$$C_6H_5.NH_2 + C_2H_5.OH = C_6H_4\Big\langle\begin{matrix}NH_2\\C_2H_5\end{matrix} + H_2O.$$

Homologues of phenol (see these) are produced by heating fatty alcohols, phenol and zinc chloride together. The easy formation of isobutyl benzene on heating benzene and isobutyl alcohol with $ZnCl_2$, deserves notice.

(3) Dry distillation of a mixture of aromatic acids with lime or soda-lime (p. 71); iron filings are introduced to accelerate the conduction of heat. All the carboxyl groups are split off in the reaction and the original hydrocarbons set free:—

$$\begin{aligned} C_8H_5.CO_2H &= C_6H_6 + CO_2, \\ C_6H_4(CO_2H)_2 &= C_6H_6 + 2CO_2, \\ C_8H_4(CH_3).CO_2H &= C_6H_5.CH_3 + CO_2. \end{aligned}$$

(4) Heating the oxygen derivatives, *e. g.*, phenols and ketones, with zinc dust, or with hydriodic acid and phosphorus. It is remarkable, that benzophenone, $C_6H_5.CO.C_6H_5$, for example, is readily reduced, while the opposite is true of diphenyl ether, $C_6H_5.O.C_6H_5$.

(5) The methods of obtaining benzenes synthetically from fatty compounds, especially acetylenes and ketones, have already received notice (p. 566).

(7) Dry distillation of various, non-volatile carbon compounds, *e. g.*, wood, resins, bituminous shales, and especially bituminous coal. When the vapors of volatile methane derivatives (CH_4, alcohol, ether) are conducted through tubes heated to redness, they set hydrogen free and yield acetylene, benzene and its homologues, styrolene, C_8H_8, naphthalene, C_8H_{10}, anthracene, etc. Petroleum and the tar from lignite, containing ethane hydrocarbons, do the same. A similar behavior is observed with a mixture of benzene vapor and ethylene (*Berichte*, 20, 660).

The chief and almost exclusive material in preparing benzene hydrocarbons is coal tar, which is made in such large quantities in the manufacture of gas. Distillation divides the tar into a *light* and *heavy* oil. The former boils from 60–180° and contains principally benzene, toluene, the three xylenes and trimethyl benzenes, as well as durene. As to their formation see *Berichte*, **18**, 3092; **19**, 2513.

To isolate these hydrocarbons, shake the light oil first with sulphuric acid, then with potash; wash, dry and finally fractionate over sodium. The heavy oil, boiling from 160–220°, sinks in water and comprises mainly phenol, cresol and naphthalene. In the portions of coal tar boiling at high temperatures, we have the solid hydrocarbons; naphthalene, $C_{10}H_8$, acenaphthene, $C_{12}H_{10}$, anthracene and phenanthrene, $C_{14}H_{10}$, pyrene, $C_{16}H_{10}$, chrysene, $C_{18}H_{12}$, and others. Some benzene hydrocarbons occur already formed in small amount in the naphtha varieties (p. 78) (for their recognition by means of bromine and $AlBr_3$, see *Berichte*, **16**, 2295), and in different ethereal oils (together with aldehydes, alcohols and acids).

Phenols, benzene, and its homologues (see *Cymene*, p. 577) are obtained by distilling camphor with zinc chloride, or phosphorus sulphide.

Properties.—The hydrocarbons of the benzene series are volatile liquids, insoluble in water, but soluble in alcohol and ether; some, containing only methyl groups, are solids at ordinary temperatures. They dissolve in concentrated sulphuric acid, on application of heat, to form sulphonic acids, *e. g.*, $C_6H_5.SO_3H$, from which the hydrocarbons can be reformed by dry distillation or by heating with concentrated hydrochloric acid (see benzene sulphonic acids). This reaction is the basis of a method for the separation of the benzenes and marsh gas series; it also permits of the preparation of the former in pure form. The benzenes dissolve in concentrated nitric acid, forming nitro-derivatives.

Acids are produced (aromatic acids) by oxidizing the side-chains of homologous benzenes with nitric acid, a chromic acid mixture, potassium permanganate, or ferricyanide of potassium. Energetic oxidation converts benzene into carbon dioxide; only minute quantities of benzoic and phthalic acids are formed at the time.

Chromyl chloride, CrO_2Cl_2, unites with the benzene homologues to form compounds which water converts into aromatic aldehydes (see these).

HYDROBENZENES, OR BENZENE HYDRIDES.

The normal benzenes can take 2, 4 and 6 hydrogen atoms, forming additive products (p. 567).

When heated with phosphonium iodide, they mostly yield the lower hydrides; thus, toluene yields the dihydride, $C_7H_8.H_2$, isoxylene, the tetrahydride, $C_8H_{10}.H_4$, and mesitylene, the hexahydride, $C_9H_{12}.H_6$; nearly all the benzenes, when acted on with hydriodic acid at 300° finally yield the hexahydrides. The latter are, in all probability, the so-called naphthenes, which have been isolated from Caucasian petroleum (*Berichte*, 23, Ref. 431). They are closely allied to the paraffins, boil about 12° lower than their corresponding normal benzenes, and are very slowly attacked by cold, alkaline permanganate. The partial benzene hydrides, C_6H_8, and C_6H_{10}, are readily oxidized by permanganate, and take up bromine with great ease (*Berichte*, 21, 836).

The benzene hydrides dissolve upon shaking them with fuming sulphuric acid, with liberation of carbon dioxide and sulphur dioxide, and the formation of sulpho-acids of the normal benzenes. For example, octonaphthene, C_8H_{16}, yields *m*-xylene sulphonic acid. But other oxidizing agents frequently separate the added hydrogen atoms, or the hydride is completely destroyed. Fuming nitric acid, or nitro-sulphuric acid, dissolves them in small amount (5 per cent.) to form nitro-derivatives of the normal benzenes. They are mostly burnt upon the application of heat (*Berichte*, 20, 1850). Many benzene hydrides precipitate metallic silver from boiling solutions of silver nitrate.

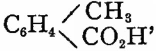
1. **Benzene**, C_6H_6, contained in coal tar, is formed by the dry distillation of all benzene acids, having only CO_2H side groups (p. 570).

That portion of the coal tar boiling from 80–85° is chilled by means of a freezing mixture, and the solid benzene then pressed out in the cold. To get perfectly pure benzene, distil a mixture of benzoic acid (1 part) and CaO (3 parts).

Common benzene from coal tar, even the purified article, invariably contains thiophene, C_4H_4S; hence it yields the indophenin reaction (p. 529). When heated with sodium it gives the reaction of Na_2S. Concentrated sulphuric acid turns it brown, and when the acid contains N_2O_3, the coloration is violet (*Berichte*, 16, 1473).

Benzene is a mobile, ethereal-smelling liquid, of specific gravity 0.899 at 0° (0.8799 at 20°). It solidifies about 0°, melts at +6°, and boils at 80.5°. It burns with a luminous flame, mixes with absolute alcohol and ether, and readily dissolves resins, fats, sulphur, iodine and phosphorus.

Benzene Hexahydride, $C_6H_6.H_6$, Hexamethylene (see above), boils at 69°; its specific gravity at 0° is 0.76.

2. **Toluene**, $C_7H_8 = C_6H_5.CH_3$, is obtained from coal tar, and is produced in the dry distillation of tolu balsam and many resins. It is synthetically prepared by the action of sodium upon C_8H_5Br and CH_3I, and by the distillation of toluic acid,  $C_6H_4{<}\begin{matrix}CH_3\\CO_2H\end{matrix}$, with lime. It is very similar to benzene, boils at 110°.3, and has a specific gravity at 0° of 0.882 (0.8656 at 20°). It does not solidify at —28°. Dilute nitric acid and chromic acid oxidize it to benzoic acid, $C_6H_5.COOH$; chromyl chloride converts it into benzaldehyde.

Ordinary, not perfectly pure, toluene contains some thiotolene, hence gives the anthraquinone reaction (p. 529) (*Berichte*, 17, 1338).

Toluene Dihydride, $C_7H_8.H_2$, boils at 105–108°. **Toluene Hexahydride**, $C_7H_8.H_6$, boils at 97°; sp. gr. 0.772 at 0°.

3. Hydrocarbons, C_6H_{10}:—

$C_6H_4(CH_3)_2$	$C_6H_5.C_2H_6$.
3 Isomerides.	1 Modification.

The three dimethyl benzenes, $C_8H_4(CH_3)_2$, or methyl toluenes (ortho, meta and para), are called

Xylenes, and occur in coal tar. Orthoxylene, with a little of the para variety, is produced on conducting CH_3Cl into benzene or toluene containing $AlCl_3$ (p. 569) (*Berichte*, 14, 2627).

That portion of coal tar oil boiling between 136–141° contains, in addition to ten per cent. paraffins, variable quantities of metaxylene (as much as 85 per cent.), paraxylene (as high as 20 per cent.), and orthoxylene (up to 20 per cent.). When the mixture is boiled with dilute nitric acid (1 part NO_3H and 3 parts H_2O) the ortho- and para- varieties are oxidized to their corresponding toluic acids, $C_6H_4(CH_3).CO_2H$, while metaxylene and the paraffins are unattacked. On shaking crude xylene with ordinary sulphuric acid, the ortho- and meta- xylenes dissolve to form sulphonic acids. Only metaxylene is dissolved if 80 per cent. sulphuric acid be used. Sodium orthoxylenesulphonate is sparingly soluble in water. Paraxylene only dissolves in fuming sulphuric acid. It also volatilizes first when crude xylene is distilled with steam (*Berichte*, 10, 1013; 14, 2625; 17, 444).

1. **Orthoxylene** (1, 2) is obtained from orthobrom-toluene by means of CH_3I and sodium, and can be prepared from toluene by means of CH_3Cl and $AlCl_3$ (*Berichte*, 14, 2628). Metaxylene is formed at the same time (*Berichte*, 18, 342). It boils at 142–143°. Dilute nitric acid oxidizes it to toluic acid, $C_6H_4(CH_3).CO_2H$; chromic acid decomposes it into carbon dioxide, and with potassium permanganate it yields phthalic acid (*Berichte*, 19, 3084).

Ortho-xylene can be nitrated by heating it for some time (6–8 hours) with a mixture of NO_3H and SO_4H_2. Bromine, at 150°, converts it into ortho-xylene bromide, $C_6H_4(CH_2Br)_2$, which melts at 94° (*Berichte*, 17, 123). On heating the three xylenes with PCl_5 in a sealed tube chlorine first enters the side-chains (*Berichte*, 19, Ref. 24). The resulting *ortho-xylylene chloride*, $C_6H_4(CH_2Cl)_2$, has also been obtained from phthalyl alcohol. The latter melts at 54°, and boils at 145° under a pressure of 20 mm.

o-**Xylene Dihydride**, C_8H_{12}, is cantharene, obtained by heating cantharides with P_2S_5. Its odor is like that of turpentine. It resinifies when exposed to the air (*Berichte*, 19, 1406).

2. **Metaxylene**, or Isoxylene (1, 3), is obtained from coal tar, and is produced from mesitylene, $C_6H_3(CH_3)_3$ (1, 3, 5), by heating mesitylenic acid, $C_6H_3\left\{\begin{matrix}CO_2H\\(CH_3)_2\end{matrix}\right.$, with lime. It could not be prepared from metabromtoluene, $C_6H_4Br.CH_3$, but was obtained in small quantity from meta-iodo-toluene. It boils at 137°; its specific gravity at 0° is 0.878. It is not oxidized by ordinary nitric acid as readily as paraxylene, and yields isophthalic acid, $C_6H_4(CO_2H)_2$. Isotoluic and isophthalic acids result from it by the action of $KMnO_4$. The hydrides are obtained by heating metaxylene or camphoric acid with HI or PH_4I: $C_8H_{10}.H_4$ and $C_8H_{10}.H_6$.

m-**Xylene Tetrahydride**, boils at 119°.

m-**Xylene Hexahydride** is identical with octonaphthene, from Caucasian petroleum. It boils at 117–118°, and when acted upon with nitric and sulphuric acids yields trinitro-isoxylene.

On warming metaxylene with fuming nitric acid a dinitro-product results, which melts at 93°. SO_4H_2 and NO_3H yield a *trinitro*-product, $C_6H(NO_2)_3.(CH_3)_2$; this melts at 176°. Characteristic amido-compounds are obtained by the reduction of the preceding nitro-derivatives. Cold, fuming nitric acid produces the *mononitro compound*, which melts at + 2° and boils at 237–239°.

3. **Paraxylene** (1, 4) is formed when camphor is distilled with $ZnCl_2$. It is obtained pure by the action of sodium and CH_3I upon parabromtoluene, $C_6H_4Br.CH_3$, or better, upon paradibrombenzene, $C_6H_4Br_2$ (*Berichte*, 10, 1356). It boils at 136–137°; its specific gravity at 19° is 0.862. Pure paraxylene solidifies in the cold, forming monoclinic needles, which melt at 15°. Dilute nitric acid oxidizes it first to paratoluic acid and subsequently to terephthalic acid, $C_6H_4(CO_2H)_2$. Chromic acid converts it immediately into the latter acid. With fuming nitric acid it yields two isomeric dinitro-paraxylenes, $C_6H_2(NO_2)_2(CH_3)_2$; the first melting at 93°, the second, more sparingly soluble in alcohol, at 123.5°. NO_3H and H_2SO_4 convert it into a trinitro-derivative, $C_6H(NO_2)_3(CH_3)_2$, which melts at 137°. The reduction of these compounds produces ill-defined amido-compounds. Paraxylene is soluble in fuming sulphuric acid only; its sulphonic acid forms large crystals, and is not very soluble.

4. **Ethyl Benzene**, $C_6H_5.C_2H_5$, is produced by the action of sodium upon C_6H_5Br and C_2H_5Br, and hydriodic acid upon styrolene, $C_6H_5.C_2H_3$, but best by the action of C_6H_5Br and $AlCl_3$ upon benzene (*Berichte*, 22, 2662). It boils at 134°. Its specific gravity at 22° equals 0.866. Dilute nitric acid and chromic acid oxidize it to benzoic acid; CrO_2Cl_2 converts it into phenyl acetaldehyde, $C_6H_5.CH_2.CHO$. It yields two liquid mononitro-products, $C_6H_4(NO_2).(C_2H_5)$

(1, 2) and (1, 4), by the action of fuming nitric acid. The first boils at 227°, the second at 245°. See p. 586 for the halogen derivatives of ethyl benzene.

4. Hydrocarbons, C_9H_{12}.

$C_6H_3(CH_3)_3$	$C_6H_4\left\{\begin{matrix}CH_3\\C_2H_5\end{matrix}\right.$	$C_6H_5.C_3H_7$.
Trimethyl Benzenes. 3 Isomerides.	Methyl Ethyl Benzenes. 3 Isomerides.	Propyl Benzenes. 2 Isomerides.

(*a*) *Trimethyl Benzenes.*

1. **Mesitylene**, symmetrical trimethyl benzene, $C_6H_3(CH_3)_3$ (1, 3, 5), occurs in coal tar, and is produced by distilling acetone, or allylene with sulphuric acid. It may, also, be prepared from phorone (p. 566).

Preparation.—Distil a mixture of acetone (1 volume) and sulphuric acid (1 volume) diluted with ½ volume of water. It is well also to add sand. The distillate consists of two layers; the upper, oily layer is siphoned off, washed with a soda solution and fractionated.

Mesitylene is an agreeable-smelling liquid, which boils at 163°. When heated with dilute nitric acid the methyl groups are successively oxidized to mesitylenic acid, uvitic acid and trimesic acid, $C_6H_3(CO_2H)_3$ (1, 3, 5). Chromic acid breaks it up, yielding acetic acid. Heated up to 280° with PH_4I we get the *hexa-hydride*, $C_9H_{12}.H_6$, boiling at 138°, and yielding the same products as mesitylene when oxidized. Warm fuming nitric acid converts it into trinitromesitylene.

Nitromesitylene, $C_9H_{11}(NO_2)$, is obtained by the nitration of mesitylene in glacial acetic acid; it melts at 44°. *Dinitromesitylene* melts at 86°. The *trinitro-compound*, obtained by adding mesitylene to a cold mixture of NO_3H and SO_4H_2, crystallizes from benzene in large, colorless needles. It dissolves in hot alcohol, but not readily in ether, and melts at 232°.

$C_6H_2Cl(CH_3)_3$ boils at 205°. $C_6HCl_2(CH_3)_3$ melts at 59° and boils at 244°. $C_6Cl_3(CH_3)_3$ melts at 204°.

$C_6H_2Br(CH_3)_3$ solidifies at 0° and boils at 225°. $C_6HBr_2(CH_3)_3$ melts at 60°, $C_6Br_3(CH_3)_3$ at 224°.

The symmetrical structure of mesitylene renders it impossible to have isomerides in these substitution products (*Annalen*, 179, 163).

Bromine, acting upon boiling mesitylene, produces the *bromides*, $C_6H_3(CH_3)_2.CH_2Br$, $C_6H_3(CH_3)(CH_2Br)_2$, and $C_6H_3(CH_2Br)_3$; the latter melts at 94° (*Berichte*, 19, Ref. 25).

2. Pseudocumene, $C_6H_3(CH_3)_3$ (1, 3, 4), unsymmetrical trimethyl benzene, occurs with mesitylene in coal tar (boiling at 162–168°) in about equal amount. It cannot, however, be separated by fractional distillation.

To separate these two hydrocarbons, dissolve the mixture in concentrated sulphuric acid and dilute with water, when the more sparingly soluble cumene-sulphonic acid will separate in the form of crystals, while mesitylene-sulphonic acid continues in solution (*Berichte*, 9, 258). The hydrocarbons are obtained by heating the sulpho-acids with hydrochloric acid to 175° (p. 571).

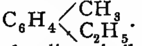
It may be synthesized by the action of sodium and CH_3I upon bromparaxylene (1, 4) and brom-metaxylene (1, 3), hence the structure (1, 3, 4). It appears in small quantities when phorone is heated with P_2O_5 or $ZnCl_2$. Pseudocumene boils at 166°. Nitric acid oxidizes it to xylic acid, so-called paraxylic acid, and finally to xylidic acid, $C_6H_3(CH_3)(CO_2H)_2$ (see these).

A mixture of NO_3H and H_2SO_4 converts pseudocumene into a *trinitro-compound*, $C_6(NO_2)_3.(CH_3)_3$, which is not very soluble in alcohol, but crystallizes from benzene in thick prisms, melting at 185°. It yields, by reduction with hydrogen sulphide, nitro-cumidine sulphonic acid (*Berichte*, 20, 966). The gradual addition of bromine to cold pseudocumene results in the formation of a crystalline *monobromide* (melting at 73°); the addition of any more reagent makes the product liquid, and it finally becomes the solid tribromide, $C_6Br_3(CH_3)_3$, melting at 224°. Sulphuric acid converts the crystalline symmetrical brom-cumene into the liquid variety (1, 2, 3, 4) (*Berichte*, 22, 1580, 1586).

When crude pseudocumene, from coal tar, is poured into a mixture of fuming NO_3H and SO_4H_2 a crystalline mass is formed; it contains three trinitro-cumenes. Crystallized from benzene the mesitylene derivative separates first in long needles, then follows the pseudocumene in thick prisms.

Hexahydro-pseudocumene, $C_9H_{12}.H_6$, is the nono-naphthene, C_9H_{18}, isolated from Caucasian petroleum. It boils at 135–138°. Its sp. gr. is 0.7812. It forms pseudocumene sulphonic acid by solution in fuming sulphuric acid. Bromine converts it into tribrom-pseudocumene (*Berichte*, 23, Ref. 431).

3. **Hemimellithene**, $C_6H_3(CH_3)_3$ (1, 2, 3), adjacent trimethyl benzene, is obtained from *a*-isodurylic acid, $C_6H_2(CH_3)_3.CO_2H$, and boils at 168–170°. It is contained in coal tar (*Berichte*, 19, 2517), and may be synthesized by the action of metallic sodium and methyl iodide upon brom-*m*-xylene.

(*b*) **Ethyl Toluenes**,  $C_6H_4\genfrac{<}{}{0pt}{}{CH_3}{C_2H_5}$. *o-Ethyl Toluene*, from *o-bromtoluene* by means of ethyl bromide and sodium, boils at 160° C. The (1, 4)-compound from parabromtoluene, boils at 161–162°, and when oxidized yields paratoluic and terephthalic acids. The (1, 3)-ethyl toluene, from metabrom-toluene, boils at 150°. It yields isophthalic acid on oxidation.

(*c*) **Propyl Benzenes**, $C_6H_5.C_3H_7$. *Normal propyl benzene*, obtained from C_6H_5Br, propyl iodide or bromide and sodium, or from benzyl chloride, $C_6H_5.CH_2Cl$, by the action of zinc ethide, boils at 157°; its specific gravity is 0.881 at 0°. In the cold bromine converts it into parabrom-propyl benzene, $C_6H_4Br.C_3H_7$, boiling at 220°. Normal cumic acid is obtained from this by the action of sodium and CO_2 (*Berichte*, 15, 698). If it be treated while hot, with bromine, we get $\beta\gamma$-dibrom-propyl-benzene, $C_6H_5.CHBr.CHBr.CH_3$ (*Berichte*, 17, 709). Propyl benzene yields phenyl-propionic aldehyde, $C_6H_5.CH_2.CH_2.CHO$, when acted upon with chromyl chloride.

Isopropyl Benzene, $C_6H_5.C_3H_7$, called **Cumene**, is made by distilling cumic acid with lime, and by the action of $AlBr_3$ upon a mixture of benzene with isopropyl bromide or normal propyl bromide. In the latter instance the normal propyl group sustains a transposition (p. 577). Normal and isopropyl chlorides also yield it. Its production from benzal chloride, $C_6H_5.CHCl_2$, by means of zinc methide, proves that the isopropyl group is present in it. Cumene boils at 153°; its specific gravity is 0.879 at 0°. Parabrom-cumene, $C_8H_4Br.C_3H_7$, yields common cumic acid, $C_6H_4(C_3H_7).CO_2H$, with sodium and CO_2. In the animal organism normal propyl benzene is oxidized to benzoic acid, while isopropyl benzene yields propyl phenol (*Berichte*, 17, 2551).

Nitric acid or the chromic acid mixture oxidizes both propyl benzenes to benzoic acid.

4. *Hydrocarbons*, $C_{10}H_{14}$:—

$C_6H_2(CH_3)_4$	$C_6H_3\left\{\begin{matrix}C_2H_5\\(CH_3)_2\end{matrix}\right.$	$C_6H_4\left\{\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right.$	$C_6H_4\left\{\begin{matrix}C_3H_7\\CH_3\end{matrix}\right.$	$C_6H_5.C_4H_9$.
3 Isomerides.	6 Isomerides.	3 Isomerides.	6 Isomerides.	4 Isomerides.

(*a*) **Tetramethyl Benzenes**, $C_6H_2(CH_3)_4$. Symmetrical **Durene** (1, 2, 4, 5) is formed from brom-pseudo cumene, $C_6H_2Br(CH_3)_3$, and dibromisoxylene, $C_6H_2Br_2(CH_3)_2$, by means of CH_3I and sodium; and from toluene by CH_3Cl and $AlCl_3$ (*Annalen*, 216, 200). It is present also in coal tar (*Berichte*, 18, 3034). It is crystalline, possesses a camphor-like odor, melts at 79–80° and boils at 190°. Nitric acid oxidizes it to durylic and cumidic acids, $C_6H_2(CH_3)_2.(CO_2H)_2$ (the symmetrical constitution of durene is concluded from this (*Berichte*, 11, 31). **Monobrom-durene**, $C_6HBr(CH_3)_4$, melts at 61°, and boils at 263°. It sustains a peculiar transposition into dibrom-durene and pentamethylbenzene, when it is shaken with ordinary sulphuric acid (*Berichte*, 20, 2837). *Dibrom-durene* melts at 199°; *dinitrodurene*, $C_6(NO_2)_2(CH_3)_4$, at 205°. Durene is but slightly dissolved on shaking with concentrated sulphuric acid. When it is heated to 100° it sustains a peculiar transformation with the production of hexamethyl benzene, the sulphonic acids of prehnitol, pseudocumene and isoxylene, which can be separated by means of their amides (*Berichte*, 20, 902). Penta-methyl and penta-ethyl benzene undergo similar transpositions (p. 578).

Unsymmetrical **Isodurene** (1, 3, 5, CH_3) is obtained from brom-mesitylene with CH_3I and Na, and from mesitylene by means of CH_3Cl and $AlCl_3$, together with durene (*Berichte*, 18, 338). It boils at 195° and does not solidify in the cold. *Dibromisodurene* melts at 209°, *dinitroisodurene* at 156°. The oxidation of isodurene with nitric acid yields three isodurylic acids, $C_6H_2(CH_3)_3.CO_2H$ (*Berichte*, 15, 1853), and at last mellophanic acid.

Adjacent tetramethyl benzene, called **Prehnitol** (1, 2, 3, 4), is produced by the action of methyl iodide and metallic sodium upon brompseudocumene and dibrom-metaxylene (*Berichte*, 21, 2821), and on warming durene with concentrated sulphuric acid (see above). It is separated from its sulpho-acid by heating with hydrochloric acid (*Berichte*, 21, 904). It is a liquid, boiling at 204°. It can only be soldified by a freezing mixture; it then melts at —4° C. Its oxidation by nitric acid produces prehnitylic acid, $C_6H_2(CH_3)_3.CO_2H$ (*Berichte*, 19, 1214) and phrenitic acid, $C_6H_2(CO_2H)_4$.

The tetramethyl benzene (*Berichte*, 19, 1553), derived from brompseudocumene, is probably identical with prehnitol.

(*b*) Symmetrical **Ethyldimethyl Benzene**, $C_6H_3\left\{\begin{matrix}(CH_3)_2\\C_2H_5\end{matrix}\right.$ (1, 3, 5), is produced (simultaneously with methyl diethyl benzene) by distilling a mixture of dimethyl ketone and methyl ethyl ketone with sulphuric acid (p. 566). It boils at 185° and is converted into mesitylenic and uvitic acids by nitric acid. *Methyl-diethyl Benzene*, $C_6H_3\left\{\begin{matrix}CH_3\\(C_2H_5)_2\end{matrix}\right.$ (1, 3, 5), which is formed at the same time, boils at 198–200°.

Two isomeric **Ethyldimethyl Benzenes** (Laurenes) are obtained by heating camphor with $ZnCl_2$ or iodine. They boil at 183–190° (see *Berichte*, 23, 983, 2349).

(*c*) **Diethyl Benzenes**, $C_6H_4(C_2H_5)_2$. *o*-**Diethyl Benzene**, from *o*-dichlorbenzene and ethyl bromide, boils at 184°. *m*-**Diethyl Benzene** is (with the para) obtained by the action of $AlCl_3$ upon benzene and ethylbromide. It boils at 182°, and when oxidized with nitric acid yields *m*-ethylbenzoic acid and isophthalic acid. *p*-**Diethyl Benzene**, from *p*-bromethyl benzene and *p*-dibrombenzene, boils at 181°. It yields *p*-ethylbenzoic acid and terephthalic acid.

(*d*) **Methylpropyl Benzenes,** $C_6H_4\left\{\begin{matrix}CH_3\\C_3H_7\end{matrix}\right.$. Those of the six possible isomerides, having the normal propyl group, are designated *cymenes* and those with the isopropyl group, *isocymenes.*

Orthocymene (1, 2) is formed from orthobromtoluene and propyl iodide, by the action of sodium, and boils at 181–182°.

Metacymene (1, 3) is formed from metabromtoluene and propyl iodide, and boils at 176–177°. **Metaisocymene** (1, 3) occurs in resin and is formed from toluene and isopropyl iodide in the presence of $AlCl_3$. It boils at 171–175° and is oxidized to isophthalic acid by chromic acid. Consult *Berichte*, 16, 2748, and *Annalen*, 235, 275, for the sulphonic acids.

Para-cymene, $C_6H_4\left\{\begin{matrix}CH_3\\C_3H_7\end{matrix}\right.$ (1, 4) methyl normal propyl benzene. This is usually called **cymene** and occurs in Roman caraway oil (from *Cuminum cyminum*), together with cumic aldehyde, and in other ethereal oils. It is produced on heating thymol and carvacrol,

$$C_6H_3(OH).(CH_3).C_3H_7,$$

with P_2S_5, or with PCl_5 and sodium amalgam; also by heating camphor, $C_{10}H_{16}O$, and some of its isomerides with P_2S_5 (along with meta-isocymene, *Berichte*, 16, 791 and 2259), or with P_2O_5 (in pure state). When camphor is heated with $ZnCl_2$, it gives rise to a series of benzene homologues, but, as it seems, no cymene, *Berichte*, 16, 624 and 2555). Cymene is obtained from turpentine oil and other terpenes, $C_{10}H_{16}$, by the withdrawal of two hydrogen atoms. This is effected by heating with SO_4H_2 or, better, with iodine, or by the action of alkalies or aniline upon the dibromide, $C_{10}H_{16}Br_2$. The production of cymene on boiling cumic alcohol, $C_6H_4(C_3H_7).CH_2.OH$ (having the isopropyl group), with zinc dust is especially interesting. A transformation of the isopropyl group takes place. Cymene may be synthetically prepared from parabrom-toluene, $C_6H_4Br.CH_3$, by means of normal propyl iodide and sodium.

Preparation.—Take a mixture of equal parts of camphor and P_2O_5 and heat until the reaction ceases. The cymene produced is poured off, again boiled with a little P_2O_5 and then distilled over sodium (*Annalen*, 172, 307). Or, shake Roman caraway-oil with a concentrated sodium bisulphite solution, which also dissolves the cumic aldehyde contained in the oil. The oil is separated and then fractionated.

Cymene is a pleasantly-smelling liquid, that boils at 175–176°; its specific gravity at 0° is 0.8722. It exhibits a characteristic absorption spectrum. It dissolves in concentrated sulphuric acid on warming, and forms a sulphonic acid. The characteristic barium salt, $(C_{10}H_{13}SO_3)_2Ba + 3H_2O$, crystallizes in shining leaflets.

Dilute nitric acid or the chromic acid mixture oxidizes cymene to paratoluic acid, $C_6H_4(CH_3).CO_2H$, and terephthalic acid; whereas in the animal organism or upon shaking with caustic soda and air, it is, strange to say, converted into cumic acid, $C_6H_4(C_3H_7).CO_2H$ (with the isopropyl group). The propyl group is converted into the isopropyl group. Similarly, the same oxy-propyl-sulpho-benzoic acid, $C_6H_3(C_3H_6.OH)\left\{\begin{matrix}CO_2H\\SO_3H\end{matrix}\right.$, as that obtained from para-isocymene sulphonic acid, is produced by the action of MnO_4K upon cymene sulphonic acid. The latter contains the normal propyl group, which was changed to the isopropyl group, then further oxidized to oxy-isopropyl, $(CH_3)_2.C(OH)$. Nitrocymene and nitroisocymene, $C_6H_3(NO_2)\left\langle\begin{matrix}CH_3\\C_3H_7\end{matrix}\right.$, yield the same nitro-oxy-isopropyl benzoic acid, $C_6H_3(NO_2)\left\langle\begin{matrix}CO_2H\\C_3H_6.OH\end{matrix}\right.$ (*Berichte*, 21, 2231).

On the other hand, ethyl propyl benzene, isopropyl-propyl benzene, acetopropyl benzene, $C_6H_4\left\langle\begin{matrix}CO.CH_3\\C_3H_7\end{matrix}\right.$ (*Berichte*, 21, 2224), and allied compounds are oxidized to normal cumic acid, $C_6H_4(C_3H_7).CO_2H$, and the propyl group remains undisturbed. In oxidations of this character, the rearrangement of the propyl to the isopropyl group takes place, if the second group oxidized is methyl, but not when ethyl, propyl and acetyl are oxidized (see Fileti, *Berichte*, 20, Ref. 168; Widmann, *Berichte*, 22, 2280; 23, 3081).

When concentrated nitric acid acts upon cymene, the product is not nitrocymene, but *p*-tolylmethylketone (*Berichte*, 19, 558; 20, Ref. 373).

Para-isocymene (1, 4) could not be made from parabrom-toluene and isopropyl iodide, but may be prepared from parabrom-cumene, $C_6H_4Br.C_3H_7$, by means of methyl iodide and sodium. It resembles paracymene in odor and boils at 171–172°; its specific gravity is 0.870 at 0°.

(*e*) **Butyl Benzenes**, $C_6H_5.C_4H_9$. *Normal butyl benzene* boils at 180°. *Isobutyl benzene* at 167°. They are obtained from brom-benzene by means of the butyl bromides, and from benzyl chloride, $C_6H_5.CH_2Cl$, by propyl and isopropyl iodides. When benzene is quickly heated to 300° with isobutyl alcohol isobutyl benzene is formed (*Berichte*, 15, 1425). The *secondary butyl benzene*, $C_6H_5.CH(CH_3)C_2H_5$, is formed from β-bromethyl benzene (p. 586) by means of zinc ethyl. It boils at 171°. The three butyl benzenes yield benzoic acid when they are oxidized.

Tertiary Butyl Benzene, $C_6H_5.C(CH_3)_3$, trimethyl phenyl methane, may be obtained from benzene by the action of isobutyl chloride and $AlCl_3$ upon it. It boils at 168°. Bromine does not attack it even when exposed to sunlight. This behavior distinguishes it from its three isomerides (*Berichte*, 23, 2412).

The following higher benzene homologues may be mentioned:—

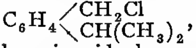
Pentamethyl Benzene, $C_6H(CH_3)_5$, is produced together with hexamethyl benzene when $AlCl_3$ and methyl chloride act upon benzene, toluene, xylene, mesitylene, etc. (*Berichte*, 20, 896). It is crystalline, melts at 51.5° and boils at 231°. Concentrated sulphuric acid dissolves it, and it then undergoes a change similar to that of durene (p. 576); hexamethyl benzene and prehnitol sulphonic acid are produced:—

$$2C_6H(CH_3)_5 + SO_4H_2 = C_6(CH_3)_6 + C_6H(CH_3)_4.SO_3H + H_2O.$$

Chlorsulphonic acid, SO_3ClH, converts it into the sulphone and the sulpho-acid of pentamethyl benzene (*Berichte*, 20, 869). The remaining H-atom can be readily substituted by acetyl, carboxyl, etc. (*Berichte*, 22, 1218).

Isoamyl Benzene, $C_6H_5.C_5H_{11}$, boils at 193°. **Amyl Benzene**, $C_6H_5.C_5H_{11}$, from benzyl bromide, $C_6H_5.CH_2Br$, and butyl bromide, boils at 201°.

Hexamethyl Benzene, $C_6(CH_3)_6 = C_{12}H_{18}$, is formed, together with the preceding (*Berichte*, 20, 896), by the polymerization of crotonylene, $CH_3.C⋮C.CH_3$, on shaking with sulphuric acid (p. 566), and by heating xylidene hydrochloride and methyl alcohol to 300° (p. 568). It crystallizes from alcohol in plates or prisms, melts at 169°, and boils at 264°. It does not dissolve in sulphuric acid, as it is incapable of forming a sulpho-acid. Potassium permanganate oxidizes it to benzene hexacarboxylic acid, $C_6(CO_2H)_6$ (mellitic acid).

Dipropyl Benzene, $C_6H_4(C_3H_7)_2$ (1, 4), is formed from paradibrom-benzene and propyl iodide, and boils at 219°. When oxidized with dilute nitric acid it forms parapropyl benzoic acid, $C_6H_4(C_3H_7).CO_2H$ (normal cumic acid). **Propyl-isopropyl Benzene**, $C_6H_4(C_3H_7)C_3H_7$, derived from cumyl chloride,  $C_6H_4\begin{cases}CH_2Cl\\CH(CH_3)_2\end{cases}$, and zinc ethyl, boils at 212°, and also yields parapropyl benzoic acid when oxidized with nitric acid.

Symmetrical Triethyl Benzene, $C_6H_3(C_2H_5)_3$ (1, 3, 5), is made by distilling ethyl-methyl ketone, $C_2H_5.CO.CH_3$, with sulphuric acid (p. 566) and by the action of ethylene and $AlCl_3$ upon benzene. It boils at 218°, and yields trimesic acid with chromic acid.

v-**Tetraethyl Benzene**, $C_6H_2(C_2H_5)_4 = C_{14}H_{22}$ (1, 2, 3, 4), is obtained from benzene, C_2H_5Br, and $AlCl_3$, and from penta-ethyl-benzene by the action of sulphuric acid. It is liquid and boils at 251°. It yields phrenitic acid, $C_6H_2(CO_2H)_4$, when oxidized with MnO_4K.

Normal **Octyl Benzene**, $C_6H_5.C_8H_{17} = C_{14}H_{22}$, from brom-benzene and normal octylchloride, boils at 262–264°, and solidifies in the cold. It yields benzoic acid when oxidized (*Berichte*, 19, 2717).

Pentaethyl Benzene, $C_6H(C_2H_5)_5$, from benzene by the action of ethyl bromide and $AlCl_3$, is a thick oil, boiling at 277°. Chlorsulphonic acid converts it into a sulpho-acid. When it is shaken with concentrated sulphuric acid it yields tetra- and hexa-ethyl benzene (*Berichte*, 21, 2814).

Hexaethyl Benzene, $C_6(C_2H_5)_6 = C_{18}H_{30}$, crystallizes in large prisms, melting at 126°, and boils at 305°.

Hexadecyl Benzene, $C_6H_5.C_{16}H_{31}$, and **Octodecyl Benzene**, $C_6H_5.C_{18}H_{37}$, are obtained by the action of hexadecyl iodide and octodecyl iodide upon iodobenzene. The first melts at 27°, and boils at 230° under a pressure of 15 mm.; the second melts at 36° and boils at 249°, under a pressure of 15 mm. (*Berichte*, 21, 3181).

HALOGEN DERIVATIVES.

The hydrocarbons of the aromatic series are more rapidly substituted by chlorine and bromine than the paraffins. In the benzene homologues the substitution occurs both in the residue and in the side groups:—

$$C_6H_3Cl_2.CH_3,\quad C_6H_4Cl.CH_2Cl,\quad C_6H_6.CHCl_2.$$

In the nucleus the halogen atoms are very firmly attached, and are not displaced by the action of KOH, silver oxide, ammonia, or sodium sulphite. The readiness with which they react with piperidine is interesting and remarkable (*Berichte*, **21**, 2279). If nitro-groups enter, then the halogens become more reactive. The halogen atoms in the side-chains behave as in the fatty bodies.

The transpositions, that various chlor- and brom-derivatives of the alkylbenzenes sustain when shaken with sulphuric acid, are worthy of note (*Berichte*, 23, 2318).

The methods of forming the halogen products are perfectly analogous to those in the fatty-series (p. 90).

(1) Bromine and chlorine manifest an interesting deportment in their substitution. In the cold and in presence of iodine, $MoCl_5$ or Fe_2Cl_6 (also when heated), they act on the nucleus only; from toluene, $(C_6H_5.CH_3)$, $C_6H_4Cl.CH_3$, $C_6H_4Br.CH_3$, and other products are obtained (*Berichte*, 13, 1216). On the other hand, on conducting chlorine or bromine vapors into boiling toluene (and its homologues), the side-chains are almost exclusively substituted; $C_6H_5.CH_2Cl$, $C_6H_5.CHCl_2$ and $C_6H_5.CCl_3$ are obtained. Acting in the warm and cold alternately (or in presence of iodine), we can substitute hydrogen atoms in the side-chains or in the nucleus (Beilstein).

It is only in exceptional cases that iodine acts substitutingly (p. 91).

Sunlight has the same effect as heat. Chlorine and bromine then, in nearly all instances, act upon the side-chains (Schramm, *Berichte*, 18, 608; 19, 214). Ferric chloride is also a carrier of bromine and chlorine (p. 91); it is also applicable in iodation (*Annalen*, 231, 195). Nitrobenzene, $C_6H_5NO_2$, may be substituted in this way.

When the homologous benzenes are heated in sealed tubes, together with PCl_5, the side-chains are alone substituted (*Berichte*, **19**, Ref. 24).

The action of chlorine and bromine slowly diminishes with the number of halogen atoms already introduced. For further chlorination, the substances must be heated with phosphorus chloride, molybdenum chloride, or iodine chloride (*Berichte*, 8, 1296). In such energetic chlorinations the side-chains of the benzene homologues are at last severed. Thus, from toluene, xylene, cumene, cymene, etc., we finally obtain perchlorbenzene, C_6Cl_6, while the side groups disappear as CCl_4. Naphthalene, anthracene, phenanthrene, and many other benzene compounds behave similarly (*Berichte*, 16, 2869). A like decomposition occurs on heating with bromine containing iodine; C_6Br_6 and CBr_4 are formed in this instance. Bromine reacts similarly, but more readily, in the presence of Al_2Br_6 (*Berichte*, 16, 2891); from cymene we get $C_6Br_5.CH_3$ and isopropyl iodide.

(2) Action of the phosphorus haloids upon the phenols and aromatic alcohols (p. 558); here both the hydroxyls in the nucleus and in the side-chains are replaced by halogens (p. 91):—

$$C_6H_4\left\{\begin{matrix}CH_3\\OH\end{matrix}\right. + PCl_5 = C_6H_4\left\{\begin{matrix}CH_3\\Cl\end{matrix}\right. + POCl_3 + HCl,$$

$$C_6H_5.CH_2.OH + PCl_5 = C_6H_5.CH_2Cl + POCl_3 + HCl.$$

(3) An important method, and one that is only applicable in the case of benzene derivatives, consists in the transformation of the diazo-compounds (see these). The diazo-group can be replaced by chlorine, bromine and iodine by various reactions. This behavior serves to substitute the halogens for nitro- and amido-groups through the agency of diazo·compounds:—

$$\underset{\substack{\text{Nitro-}\\\text{benzene.}}}{C_6H_5.NO_2} \text{ yields } \underset{\substack{\text{Amido-}\\\text{benzene.}}}{C_6H_5.NH_2}, \quad \underset{\substack{\text{Diazo-}\\\text{benzene.}}}{C_6H_6.N_2X} \text{ and } \underset{\text{Benzene Haloid.}}{C_6H_5(Cl, Br, I)}.$$

Halogen products can be obtained from substituted amido-compounds by introducing hydrogen for the amido-group through the diazo-derivative:—

$$C_6H_3Br_2.NH_2 \text{ yields } C_6H_4Br_2.$$

(4) Decomposition of substituted acids by heating them with lime (p. 570):—

$$\underset{\text{Chlorbenzoic Acid.}}{C_6H_4Cl.CO_2H} = \underset{\text{Chlorbenzene.}}{C_6H_6Cl} + CO_2.$$

Additive products are obtained by letting an excess of chlorine or bromine act upon benzene or the chlor-benzenes, in the sunlight (p. 567):—

$$\begin{array}{lll} C_6H_6.Cl_2 & C_6H_6.Cl_4 & C_6H_6.Cl_6 \\ C_6H_5Cl.Cl_2 & C_6H_5Cl.Cl_4 & C_6H_6Cl.Cl_6, \text{ etc.} \end{array}$$

Hexachlorbenzene, $C_6H_6Cl_6$, is also formed by conducting chlorine into boiling benzene; substitution products are produced at the same time. The additive products are solids, and do not volatilize without decomposition. When distilled or heated with alkalies, half of the added chlorine (or bromine) breaks off as hydrogen chloride (or bromide):—

$$C_6H_6Cl.Cl_4 = C_6H_3Cl_3 + 2HCl.$$

Protracted action of sodium amalgam upon the alcoholic solutions of the halogens brings about the substitution of hydrogen for the halogens. Heating with hydriodic acid and phosphorus effects the same result.

BENZENE DERIVATIVES.

Monochlor-benzene, C_6H_6Cl, phenyl chloride (the group C_6H_5 is called phenyl), is obtained from benzene, and from phenol, $C_6H_5.OH$, by the action of PCl_6 upon the latter. It boils at 132° and solidifies at —40°; its sp. gr. at 0° is 1.128.

Dichlor-benzenes, $C_6H_4Cl_2$. In the chlorination of benzene the products are chiefly solid para- and a little liquid ortho-dichlor-benzene.

Paradichlor-benzene (1, 4) forms monoclinic needles, melts at 56°, and boils at 173°. It is obtained also by the action of PCl_5 on para-nitraniline, parachlorphenol and para-phenol-sulphonic acid. It forms a mononitro-product, $C_6H_3Cl_2.NO_2$ (1, 4, NO_2), melting at 55°.

Metadichlor-benzene (1, 3), from metachlor-aniline, β-dichlor-aniline, $C_6H_3Cl_2.NH_2$, and common dinitro-benzene, is a liquid, and boils at 172°. Its mononitro-derivative melts at 32° (1, 3, 4 — NO_2 in 4).

Orthodichlor-benzene (1, 2), from benzene and orthochlor-phenol, is a liquid, and boils at 179°; its nitro-derivative melts at 49° (1, 2, 4 — NO_2 in 4).

Trichlor-benzenes, $C_6H_3Cl_3$.

Ordinary trichlor-benzene (1, 2, 4) is produced in the chlorination of benzene, or the three dichlor-benzenes, and is also obtained from benzene hexachloride, and α-dichlor-phenol. It melts at 17°, and boils at 213°. Its nitro-compound (1, 2, 4, 5 — NO_2 in 5) melts at 58°.

Symmetrical Trichlor-benzene (1, 3, 5) is obtained from ordinary trichlor-aniline and from $C_6H_6Cl.Cl_4$. Long needles, melting at 63.5°, and boiling at 208°.

The *adjacent* trichlor-benzene (1, 2, 3) is formed from trichlor-aniline (1, 2, 3, 4). It consists of plates which dissolve with difficulty in alcohol, melt at 54°, and boil at 218° (*Annalen*, 192, 228).

Tetrachlor-benzenes, $C_6H_2Cl_4$.

Ordinary (symmetrical) tetrachlor-benzene (1, 2, 4, 5) is produced in the chlorination of benzene, or is obtained from the nitro-derivative of common trichlor-benzene (melting at 58°). It melts at 138°, and boils at 243–246°. Boiled with nitric acid it yields chloranil, $C_6Cl_4O_2$ (O_2 = 1, 4). The unsymmetrical tetrachloride (1, 3, 4, 5) = (1, 2, 4, 6) is formed from ordinary trichlor-aniline, and consists of needles, melting at 51°, and boiling at 246°.

The *adjacent* tetrachlor-benzene (1, 2, 3, 4) is formed from *adjacent* trichlor-aniline (from metachlor-aniline), and consists of long needles, melts at 46°, and boils at 254° (*Annalen*, 192, 236).

Pentachlor-benzene, C_6HCl_5, can only exist in one modification. It is produced by chlorination; forms needles, which melt at 86°, and boil at 276°.

Hexachlor-benzene, C_6Cl_6, is produced in the chlorination of benzene and other compounds (p. 580) in the presence of $SbCl_5$ or ICl_3, and when $CHCl_3$ or C_2Cl_4 are conducted through tubes heated to redness. It melts at 226°, and boils at 332°. It forms perchlorphenol when heated to 250° with caustic potash (*Berichte*, 18, 335).

Benzene Hexachloride, $C_6H_6Cl_6$, obtained by the action of chlorine upon benzene in sunlight, or upon boiling benzene, melts at 157°. When it is distilled, it decomposes into $C_6H_3Cl_3 + 3HCl$. See *Berichte*, 18, Ref. 149, for an isomeric hexachloride.

Monobrom-benzene, C_6H_5Br, from benzene and phenol, boils at 155°; its specific gravity at 0° is 1.517.

Dibrom-benzenes, $C_6H_4Br_2$. When bromine acts upon benzene (on heating) (*Berichte*, 10, 1354), it is chiefly the para- and little of the ortho- that results. *p-Dibrom-benzene* (1, 4), from benzene, parabrom-phenol and para-bromaniline, melts at 89°, and boils at 218°. Its mononitro-derivative (1, 4, NO_2) melts at 85°. *m-Dibrom-benzene* (1, 3), from ordinary dinitro-benzene and dibrom-aniline, does not solidify at —20°, and boils at 219°. It yields two mononitro-products, one of which melts at 61° (1, 3, 4 — NO_2 in 4) (chief product), the other (1, 3, 2 — NO_2 in 2), at 82.5°. *o-Dibrom-benzene* (1, 2), from orthonitraniline and orthonitro-brom-benzene, becomes solid below 0°, melts at —1°, and boils at 224°. Its nitro-product (1, 2, 4 — NO_2 in 4) melts at 58.6°.

Tribrom-benzenes, $C_6H_3Br_3$. Körner was the first to make a comprehensive investigation of these derivatives with respect to their relations to the three dibrom-benzenes, and to examine into their structure (p. 562).

Ordinary unsymmetrical tribrom-benzene (1, 3, 4) is obtained directly from benzene by the action of bromine. It results from all three dibrom-benzenes, hence (1, 3, 4); also from $C_6H_6Br_6$, from common dibrom-phenol and from ordinary dibrom-aniline. It melts at 44°, and boils at 275°. *Symmetrical* tribrombenzene (1, 3, 5), from tribromaniline, melts at 119.5°, and boils about 278°.

The third *adjacent* tribrom-benzene (1, 2, 3) is formed like the corresponding trichlor-benzene, and melts at 87°.

Tetrabrombenzenes, $C_6H_2Br_4$. The common variety results from the treatment of benzene and nitro-benzene with bromine. It melts at 175°. The *unsymmetrical* variety (1, 3, 5, Br) is obtained from ordinary tribromaniline and ordinary tribromphenol. It melts at 97–99°, and boils near 329°.

Pentabrombenzene, C_6HBr_5, the only possible modification, is obtained by acting on benzene with bromine. It melts near 240°.

Hexabrombenzene, C_6Br_6, is formed by heating benzene (toluene. etc., p. 580) and bromine to 300–400°; or by heating CBr_4 to 300°. It consists of needles, almost insoluble in alcohol and ether; they melt above 310°.

Benzene Hexabromide, $C_6H_6Br_6$, is produced when bromine acts on benzene in sunlight. It is a crystalline compound and decomposes, when heated, into unsymmetrical tribrombenzene and HBr.

Iodo-benzene, C_6H_5I, is formed on heating benzene with iodine and iodic acid to 200°; by the action of phosphorus iodide upon phenol, and from aniline through the diazo-compound. It is a colorless liquid, boiling at 185°; its sp. gr. equals 1.69.

Di-iodo-benzenes, $C_6H_4I_2$: (1, 4) melts at 129° and boils near 280°; (1, 3) melts at 40.5° and boils at 282°; both crystallize in leaflets. (1, 2) crystallizes on cooling, melts at 27°, and boils at 286° (*Berichte*, 21, Ref. 349).

Tri-iodo-benzene, $C_6H_3I_3$, melts at 76° and sublimes readily.

Fluorbenzene, C_6H_5Fl, has been obtained from potassium fluorbenzoate. A liquid with an odor like that of benzene, and boiling at 85° (*Berichte*, 17, Ref. 109). *p-Fluortoluene*, $C_6H_4Fl.CH_3$, obtained in an analogous manner, has an odor like that of bitter almond oil, and boils at 114°. When it oxidizes it forms *p*-fluorbenzoic acid.

These fluorbenzenes are also formed in the action of concentrated hydrofluoric acid upon the benzene diazoamido-compounds with fatty residues (*Berichte*, 19, Ref. 753; 21, Ref. 96). *Fluornitrobenzene*, $C_6H_4(NO_2)Fl$ (1, 4), melts at 24° C. and boils at 205° C. *p-Difluorbenzene*, $C_6H_4Fl_2$, boils at 88°.

DERIVATIVES OF TOLUENE.

Chlortoluenes, $C_6H_4Cl.CH_3$. Para- and ortho-derivatives are produced in an almost equal amount when toluene is treated with chlorine and bromine (in the cold or in the presence of iodine (p. 580). The former is a solid and boils somewhat higher than the ortho-compounds. The haloid toluenes may be obtained pure from the amido-toluenes, by replacing the NH_2-group by halogens; this is accomplished through the diazo-compounds. Thus $C_6H_4(NH_2).CH_3$ yields $C_6H_4X.CH_3$. When heated with a chromic acid mixture (see aromatic acids) the para- and meta-derivatives (by the conversion of the CH_3-group into CO_2H) are oxidized to the corresponding substituted benzoic acids, whereas the ortho-derivatives are attacked with difficulty and completely destroyed. When boiled with dilute nitric acid, with MnO_4K, or ferricyanide of potassium, all three isomerides (even the ortho) are oxidized to acids.

Parachlortoluene, $C_6H_4Cl.CH_3$ (1, 4), solidifies at 0°, melts at 6.5° and boils at 160°. It yields parachlorbenzoic acid when oxidized with chromic acid or nitric acid. *Orthochlortoluene* (1, 2), from toluene and orthotoluidine, is liquid, and boils at 156°; chromic acid completely decomposes it. *Metachlortoluene* (1, 3) has been prepared from chlorparatoluidine, $C_6H_3Cl(NH_2).CH_6$, by replacement of NH_2 by hydrogen. It boils at 150° and yields metachlorbenzoic acid. See *Berichte*, 19, 2440 for nitrochlortoluenes.

Benzyl Chloride, $C_6H_5.CH_2Cl$, α-chlortoluene is obtained by the chlorination of boiling toluene (p. 580), and from benzyl alcohol, $C_6H_5.CH_2.OH$. It boils at 176°. The chlorine atom is readily exchanged. It passes into benzyl alcohol when boiled with water (30 parts). Heated with water and lead nitrate it yields benzaldehyde, and by oxidation benzoic acid.

When benzyl chloride is heated to 200° with water, the chloride, $C_{14}H_{13}Cl$, is produced, and by the distillation of this product, benzyl toluene, $C_6H_5.CH_2.C_6H_4.CH_3$, anthracene, $C_{14}H_{10}$, and other bodies are formed.

In the nitration of $C_6H_5.CH_2Cl$, $C_6H_5.CHCl_2$ and $C_6H_5.CCl_3$, the products are predominantly *para-nitro*-derivatives with some of the ortho. Further oxidation transforms these into nitro-benzoic acids (*Berichte*, 17, 385 and *Annalen*, 224, 100). From $C_6H_5.CHO$, $C_6H_5.CO.CH_3$, $C_6H_5.CO_2H$ and $C_6H_5.CN$, we obtain meta-products principally. *o*- and *p*-Nitrobenzyl chlorides are also obtained by the chlorination, at a boiling temperature, of *o*- and *p*-nitrotoluenes; the *o*- and *m*-chlorides are more easily produced by the action of PCl_5 upon *o*- and *m*-nitrobenzyl alcohol (*Berichte*, 18, 2402).

o-Nitrobenzyl chloride, $C_6H_4(NO_2).CH_2Cl$, melts at 49°; the meta- at 45–47°; the para at 73° C. Pyrogallol reduces the latter to nitrotoluene. For its derivatives see *Berichte*, 23, 337.

Dichlortoluenes, $C_7H_6Cl_2$:—

$C_6H_3Cl_2.CH_3$	$C_6H_4Cl.CH_2Cl$	$C_6H_5.CHCl_2$.
Dichlortoluenes.	Chlorbenzyl Chlorides.	Benzal Chloride.

The first compound must have six modifications; the six corresponding dibromtoluenes have all been prepared. There must be three isomerides of the second, and of the third compound only one modification is possible.

Benzal Chloride, $C_6H_5.CHCl_2$ (Benzylene chloride, Chlorobenzene), is formed in the chlorination of boiling toluene and from oil of bitter-almonds, $C_6H_5.CHO$, by means of PCl_5. It is a liquid boiling at 206°, and has a sp. gr. 1.295 at 16°. It changes to oil of bitter-almonds when exposed to a temperature of 120° in the presence of water. Satisfactory nitro-products have not been obtained by the nitration of benzalchloride or by conducting chlorine into *p*-nitrotoluene (*Berichte*, 18, 996). *p-Nitrobenzal chloride*, $C_6H_4(NO_2).CHCl_2$, has been prepared by the action of PCl_5 upon *p*-nitrobenzaldehyde. It melts at 46°.

On heating *p*-nitrotoluene with bromine to 120–140°, *p-Nitrobenzyl bromide*, $C_6H_4(NO_2).CH_2Br$, and *p-Nitrobenzal bromide*, $C_6H_4(NO_2).CHBr_2$ are readily formed. The first melts at 100°, and the second at 82° (*Annalen*, 185, 268).

Trichlortoluenes, $C_7H_5Cl_3$:—

$C_6H_2Cl_3.CH_3$	$C_6H_3Cl_2.CH_2Cl$	$C_6H_4Cl.CHCl_2$	$C_6H_5.CCl_3$.
6 Isomerides.	6 Isomerides.	3 Isomerides.	1 Modification.

Two trichlorine derivatives, *α*- and *β*- (1, 2, 4, 5 —CH_3 in 1 and 1, 2, 3, 4), $C_6H_2Cl_3.CH_3$, are formed in chlorinating toluene; the *α*- melts at 82° and boils at 230°; the *β*- melts at 41° and boils at 232° (*Berichte*, 18, 421). In accordance with its constitution diamid-*α*-trichlortoluene is oxidized to trichlortoluquinone.

Benzotrichloride, $C_6H_5.CCl_3$, prepared from benzoyl chloride, $C_6H_5.COCl$, by action of PCl_5, is a liquid, and boils at 213°. It yields benzoic acid when heated to 100° with water.

Pentachlortoluene, $C_6Cl_5.CH_3$, melts at 218° and boils at 301°. Further chlorination leads to the substitution of the methyl group, which finally is broken off and hexachlorbenzene, C_6Cl_6 (p. 580), formed.

Monobromtoluenes, $C_6H_4Br.CH_3$.

Parabromtoluene (1,4), from toluene and paratoluidine, melts at 28.5° and boils at 185°; it yields parabrombenzoic acid.

Metabromtoluene (1, 3) is formed by acting on, $C_6H_4\begin{cases}CH_3\\NH.C_2H_3O,\end{cases}$ acetparatoluidine, with bromine, and replacing the amido-group by hydrogen; and in a similar manner from acetorthotoluidine. It boils at 184°, and yields metabrombenzoic acid. *Orthobromtoluene* (1, 2), obtained with the para- on treating toluene with bromine, and also from ortho-toluidine, boils at 182–183°; its sp. gr. at 20° is 1.40. A chromic acid mixture gradually destroys it; dilute nitric acid oxidizes it to orthobrombenzoic acid.

Benzyl Bromide, $C_6H_5.CH_2Br$, is prepared by the action of bromine upon boiling toluene, and by the action of HBr upon benzyl alcohol. It is a liquid, which provokes tears and boils at 210°; its specific gravity = 1.438 at 22°.

Dibromtoluenes, $C_6H_3Br_2.CH_3$. The six possible isomerides have been prepared in various ways (*Berichte*, 13, 970).

Benzal Bromide, $C_6H_5.CHBr_2$, from benzaldehyde, decomposes upon distillation.

o-**Brombenzyl Bromide**, $C_6H_4Br.CH_2Br$, from ortho-bromtoluene, melts at 30°, and with sodium forms anthracene and phenanthrene. Chromic acid does not oxidize it. *p-Brombenzyl Bromide*, from *p*-bromtoluene, melts at 61°.

Iodo-toluenes, $C_6H_4I.CH_3$.

Paraiodotoluene (1, 4), from paratoluidine, crystallizes in shining laminæ, melts at 35° and boils at 211°. Chromic acid converts it into paraiodobenzoic acid. *Metaiodotoluene* (1, 3), from liquid metatoluidine, is a liquid boiling at 207°, and when oxidized by chromic acid yields metaiodobenzoic acid. *Orthoiodotoluene* (1, 2), from orthotoluidine, is liquid, and boils at 205°. When oxidized with dilute nitric acid it becomes orthoiodobenzoic acid.

Benzyl Iodide, $C_6H_5.CH_2I$, is obtained from benzyl chloride by the action of hydriodic acid at the ordinary temperature. It melts at 24° and decomposes when distilled.

Ethyl Benzene Derivatives, $C_6H_5.CH_2.CH_3$.

The replacement of the hydrogen in the ethyl group gives rise to two isomeric mono- and three isomeric di-derivatives:—

$C_6H_5.CH_2.CH_2Cl$	$C_6H_5.CHBr.CH_3$
α-Chlorethyl Benzene.	*β* Bromethyl Benzene.

The α-derivatives have also been called ω-derivatives, the β- the α-derivatives.

α-**Chlorethyl Benzene** is formed in the chlorination of hot ethyl benzene. It is an oil boiling at 200–204° C., when it decomposes into hydrochloric acid and styrene. Potassium cyanide converts it into a cyanide and then hydrocinnamic acid. β-**Chlorethyl Benzene**, obtained from phenyl methyl carbinol, $C_6H_5CH(OH).CH_3$, through the action of HCl, boils at 194° C.

α-**Bromethyl Benzene**, from styrene by the action of HBr, decomposes into the latter and styrene on warming. The *β-product* is produced when ethyl benzene is brominated at a boiling temperature or in sunlight (*Berichte*, **18**, 351), and also results from the action of HBr upon phenyl methyl carbinol (see above). It does not react either with KCN or with CO_2 and sodium.

α-**Dichlorethyl Benzene**, $C_6H_5.CH_2.CHCl_2$, from phenyl-acetaldehyde and PCl_5, is an oil with penetrating odor. Alcoholic potash converts it into α-chlorstyrene (*Berichte*, 18, 982). β-**Dichlorethyl Benzene**, $C_6H_5CCl_2.CH_3$, is formed from acetophenone, $C_6H_5.CO.CH_3$, and PCl_5. αβ-**Dichlorethyl Benzene**, $C_6H_5.CHCl.CH_2Cl$, styrene chloride, from styrene by the absorption of 2Cl, yields α-chlorstyrene with alcoholic potash.

αβ-**Dibromethyl Benzene**, $C_6H_5.CHBr.CH_2Br$, styrene bromide, is produced by the action of bromine upon styrene, and by the bromination of ethyl benzene in diffused light (*Berichte*, 18, 354). It is a solid and melts at 74° C. With alcoholic potash it yields β-bromstyrene. β-**Dibromethyl Benzene**, $C_6H_5.CBr_2.CH_3$, formed by the bromination of ethyl benzene in sunlight, is a liquid.

The halogen derivatives of the higher benzenes are described in connection with these.

NITRO–DERIVATIVES.

All benzene derivatives readily pass into nitro-products (p. 105) through the action of nitric acid, the benzene nucleus (not the side-chains) being substituted :—

$$C_6H_5.CH_3 + NO_3H = C_6H_4(NO_2).CH_3 + H_2O.$$

The substance to be nitrated is gradually added to concentrated or fuming nitric acid, when it will dissolve with evolution of brown vapors. When this does not occur heat should be applied. On pouring the solution into water the nitro-products, not soluble in water, are precipitated.

A mixture of nitric acid (1 part) and sulphuric acid (2 parts) acts more energetically, as the second acid combines with any water that may be formed in the reaction.

Di- and tri-nitro-compounds are the chief products.

The nitration is considerably moderated by previously dissolving the substance in glacial acetic acid. The more alkyl groups there are in a benzene hydrocarbon, the more readily will it be nitrated. Nitric acid of sp. gr. 1.5 very frequently reacts more energetically than the acid of 1.535 sp. gr., because the latter contains more nitrogen dioxide (*Berichte*, 21, Ref. 51).

Nitro-derivatives of substituted hydrocarbons are obtained: (1) by nitration of the halogen derivatives, while in the inverse action of chlorine and bromine upon nitro-derivatives in the heat the nitro-group is generally eliminated; (2) by the action of PCl_5 and PBr_5 upon nitro-phenols, *e. g.*, $C_6H_4(NO_2).OH$, when the hydroxyl group is replaced by halogens; (3) from nitro-amido-compounds, the amido-group being exchanged for halogens through the agency of the diazo-compounds; (4) by the action of potassium nitrite and copper upon diazo-salts; (5) by decomposition of nitro-acids when heated with lime (p. 570).

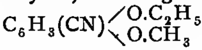
Various reducing agents convert the nitro into amido-compounds (p. 591). Sodium amalgam or alcoholic potash produces azo-compounds. The nitro-derivatives generally possess a faint yellow color; ammonia deepens the latter. The mono-nitro-benzenes usually boil undecomposed; the di-derivatives are not volatile.

DERIVATIVES OF BENZENE.

Nitro-benzene, $C_6H_5.NO_2$, is obtained by dissolving benzene in a mixture of common nitric and sulphuric acids. It is a bright yellow liquid, possessing an odor resembling that of oil of bitter almonds (artificial almond oil, oil of mirbane), and a specific gravity at 0° of 1.20. It becomes crystalline at $+ 3°$ and boils at 205°.

Dinitro-benzenes, $C_6H_4(NO_2)_2$. The three dinitro-benzenes are produced, if in the nitration with fuming nitric acid, the mixture be boiled a short time. On crystallizing from alcohol, the meta-compound, formed in greatest quantity, separates first, whereas the ortho- and para-dinitro-derivatives remain in solution (*Berichte*, 7, 1372). For the production of *o*-dinitro-benzene, see *Berichte* 17, Ref. 20.

The ortho-compound (like other ortho-dinitro-benzenes) exchanges an NO_2-group for OH when boiled with caustic soda, forming *o*-nitro-phenol, $C_6H_4(NO_2).OH$. Likewise on heating ortho-dinitro-compounds with alcoholic ammonia (and with anilines), we have *o*-nitranilines, *e.g.*, $C_6H_4(NO_2).NH_2$, produced. Ferricyanide of potash and caustic soda oxidize the metadinitro-benzenes to dinitrophenols; they unite with aniline, yielding molecular compounds. *m*- and *p*-Dinitrobenzenes combine, too, with benzenes, naphthalenes, etc. (*Berichte*, 16, 234).

Meta-dinitrobenzene (1, 3) is obtained from common dinitrotoluene (1, 2, 4, CH_3 in 1), and from α- and β-dinitraniline; it was formerly called para. It crystallizes in long, colorless needles, sparingly soluble in cold alcohol, and melting at 89.9°. It boils at 297°. By reduction it yields (1, 3)-nitraniline and (1, 3)-phenylene diamine (melting at 63°). When heated with potassium ferricyanide and caustic soda, it forms α- and β-dinitrophenol, $C_6H_3(NO_2)_2.OH$. *m*-Dinitro-benzene, heated with alcoholic potash, has one of its nitro-groups removed with formation of $C_6H_3(NO_2)(O.C_2H_5).CN$, which, heated with alcoholic potash, yields dioxyethyl benzonitrile, $C_6H_3(O.C_2H_5)_2CN$. This fused with KOH, becomes dioxybenzoic acid. When paradinitrobenzene (not ortho) is boiled with alcoholic potassium cyanide potassium nitrite is also formed (*Berichte*, 17, Ref. 19). Upon digesting nitro-oxyethyl benzonitrile with potassium methylate, the nitro group is replaced and oxyethyl-oxymethyl-benzonitrile formed:  $C_6H_3(CN)\begin{smallmatrix}/O.C_2H_5\\ \backslash O.CH_3\end{smallmatrix}$ (1, 2 6, CN in 1) *Berichte*, 18, Ref. 148.

Paradinitrobenzene (1, 4) forms colorless needles, is more sparingly soluble in alcohol, melts at 173°, and yields (1, 4)-nitraniline and (1, 4)-phenylene diamine (melting at 140°).

Orthodinitro-benzene (1, 2), formed in very small amount in nitration, crystallizes in plates from hot water, and melts at 118°. It yields (1, 2)-nitraniline, and (1, 2)-phenylenediamine (melting at 99°).

Symmetrical Trinitrobenzene, $C_6H_3(NO_2)_3$ (1, 3, 5), is produced by heating meta-dinitrobenzene with HNO_3 and pyrosulphuric acid to 140°; it crystallizes in white laminæ or needles and melts at 121–122°. It becomes trinitrophenol (Picric Acid) when heated with ferricyanide of potassium and caustic soda. It unites with benzenes and anilines, forming molecular compounds (*Berichte*, 13, 2346). *p*-Dinitrobenzene forms unsymmetrical trinitrobenzene (1, 2, 4) (*Berichte*, 17, Ref. 233).

Nitro-haloid Benzenes, $C_6H_4X(NO_2)$.

Upon nitrating chlor-, brom-, and iodo-benzene, para- and ortho-mononitro products result; the first in larger quantity. The meta-derivatives are prepared from meta-nitraniline, $C_6H_4(NO_2).NH_2$ (from common dinitro-benzene), by replacement of the amido group by halogens, effected by means of the diazo-compounds. The para- and ortho-compounds can be similarly prepared from the corresponding nitranilines. PCl_5 also converts nitro-phenols, $C_6H_4(NO_2).OH$, into chlornitro-derivatives. Metachlornitro-benzene is obtained by the chlorination of nitrobenzene in the presence of iodine, or $SbCl_3$.

The isomeric mononitro-chlor-, brom-, and iodo-benzenes have the following melting points:—

	(1, 2).	(1, 3).	(1, 4).
$C_6H_4Cl(NO_2)$	32.5°	44.4°	83°
$C_6H_4Br(NO_2)$	41.5°	56°	126°
$C_6H_4I(NO_2)$	49°	33°	171°.

Meta-chlornitrobenzene occurs in two physical modifications: if rapidly cooled after fusion, it melts at 23.7°, but in a short time reverts to the stable modification, melting at 44.4°.

As may be seen above, the para-derivatives possess the highest melting points, and the meta- are generally higher than the ortho. A similar deportment is manifested by almost all di-derivatives of benzene (p. 598). Again, the para-compounds usually dissolve with more difficulty in alcohol. The different behavior of chlor- and brom-nitrobenzenes with caustic potash and ammonia is very instructive. The ortho- and para-derivatives (latter with more difficulty than the former) yield the corresponding nitro-phenols, $C_6H_4.(NO_2).OH$, when heated with aqueous or alcoholic potash in closed tubes to 120°. In this reaction the halogens are replaced by hydroxyl. The meta-derivatives do not react under the above conditions. The ortho- and para-compounds also yield corresponding nitranilines, $C_6H_4(NO_2).NH_2$, when heated to 100° with alcoholic ammonia, while the (1, 3)-chlor- and brom-nitrobenzenes do not react (compare dinitrobenzene (p. 587) and the nitranilines).

In the nitration of the mono-haloid benzenes, as well as in the chlorination (bromination) of benzene (p. 580) and toluene (p. 583), the para- and ortho-compounds (1, 4) and (1, 2) are almost the only products. So in the nitration (chlorination) of phenol, $C_6H_5.OH$, of toluene, $C_6H_5.CH_3$, and of aniline, $C_6H_5.NH_2$, the first derivatives are only the ortho- and para-varieties. It is only in the nitration (chlorination) of nitrobenzene, $C_6H_5(NO_2)$, benzoic acid, $C_6H_5.CO_2H$, benzaldehyde, $C_6H_5.CHO$, benzonitrile, $C_6H_5.CN$, acetophenone, $C_6H_5.CO.CH_3$, and some additional compounds, *with negative side-chains*, that the *meta-derivatives predominate* in the presence of the ortho- and para-varieties.

Thus, from benzoic acid we get meta-nitrobenzoic acid, from nitrobenzene meta-dinitrobenzene, $C_6H_4(NO_2)_2$ (1, 3). Benzene sulphonic acid, $C_6H_5.SO_3H$, yields meta-benzene disulphonic acid, $C_6H_4(SO_3H)_2$ (1, 3). The following groups: OH, NH_2, Cl and Br, CH_3 and all alkyls cause the entering, substituting group to assume the ortho- and para-positions, and have been designated *substituents of the first class*, while the groups NO_2, CO_2H, CN, $CO.CH_3$, SO_3H, etc., are known as *substituents of the second class* (see Lellmann, *Principien der org. Synthese*, p. 11). Consult *Berichte*, **23**, 130 upon the influence exerted by the atomic magnitude of the substituents.

By the further substitution (chlorination, nitration) of the ortho- and para-di-derivatives (from compounds containing substituents of the first class) the replacing groups enter the para- or ortho-position, so that di-derivatives (1, 2) and (1, 4) yield the same tri-derivatives (1, 2, 4). *Hence, the tendency of the tri-derivatives is to form the unsymmetrical combination* (see *Annalen*, **192**, 219). The substitution relations are more complicated in the case of the meta-di-derivatives (1, 3).

If an unsymmetrical tri-derivate (1, 2, 4) be further substituted, unsymmetrical tetra-derivatives (1, 2, 4, 6) are generally produced. Thus, from aniline, $C_6H_5.NH_2$, phenol, $C_6H_5.OH$, etc., we obtain compounds like $C_6H_2Cl_3.NH_2$ and $C_6H_2(NO_2)_3.OH$ (1, 2, 4, 6—NH_2 or OH in 1), in which the entering groups occupy the meta-position ($2, 4, 6 = 1, 3, 5$) with reference to each other. By the elimination of the OH and NH_2 groups in them, we obtain symmetrical tri-derivatives, $C_6H_3X_3$ (1, 3, 5).

α-**Dinitro-chlorbenzene**, $C_6H_3Cl(NO_2)_2$ (1, 2, 4), is obtained from (1, 2)- and (1, 4)-chlornitro-benzene, or from ordinary dinitrophenol, and by the direct nitration of C_6H_5Cl. It melts at 53.4°. The nitro-groups in it hold the position (1, 3) = (2, 4).

α-**Dinitro-brombenzene**, $C_6H_3Br(NO_2)_2$ (1, 2, 4), is formed like the preceding and melts at 75.3°. When boiled with a soda-solution both yield ordinary dinitrophenol, and with alcoholic ammonia *α*-dinitraniline (melting at 182°).

The nitration of meta-chlor and bromnitro-benzene produces the isomerides *β*-**chlor- and bromdinitro-benzenes**, $C_6H_3Cl(NO_2)_2$, and $C_6H_3Br(NO_2)_2$ (1, 3, 4. Cl and Br occupy 1); the first exists in three modifications, which melt at 36.3°, 37°, and 38.8° (*Berichte*, 9, 760); the second consists of yellow plates, melting at 59.4°.

Trinitro-chlorbenzene, $C_6H_2Cl(NO_2)_3$ (1, 3, 5, Cl), **Picryl Chloride**, is obtained from picric acid by the action of PCl_5. It melts at 83°. It is converted into picramide, $C_6H_2(NH_2)(NO_2)_3$, with ammonia, and into picric acid when boiled with soda.

DERIVATIVES OF TOLUENE.

By nitration toluene yields chiefly two isomeric **nitro-toluenes**, $C_6H_4(NO_2).CH_3$, the solid para-compound and the liquid ortho-derivative. They can be separated by fractional distillation. The para-nitrotoluene predominates when the nitration occurs at an elevated temperature and fuming acid is employed, but at low temperatures, and with nitric and sulphuric acids, the ortho-body is in greater quantity (about 66 per cent.).

Paranitro-toluene (1, 4) forms large prisms; melts at 54° and boils at 237°. Chromic acid oxidizes it to paranitro-benzoic acid; paratoluidine is the product of its reduction. Chlorination at 150° produces paranitro-benzal chloride, $C_6H_4(NO_2).CHCl_2$, which forms *p*-nitro-benzaldehyde with SO_4H_2.

Orthonitro-toluene (1, 2) is liquid, and boils at 223°; its specific gravity at 23° is 1.163. It is also formed in the partial reduction of dinitro-toluene with ammonium sulphide, and the replacement of the NH_2-group of the resulting amide by hydrogen. Chromic acid destroys it, but when oxidized with HNO_3, MnO_4K, or potassium ferricyanide, orthonitro-benzoic acid is the product; it yields ortho-toluidine by reduction. Bromine added to orthonitro-toluene at 170° produces dibromanthranilic acid:—

$$C_6H_4(NO_2).CH_3 + 2Br_2 = C_6H_2Br_2(NH_2).CO_2H + 2HBr.$$

Metanitro-toluene (1, 3) is formed if acetparatoluidine, $C_6H_4\begin{cases}CH_3\\NH.C_2H_3O,\end{cases}$ is nitrated, and the amido-group replaced by hydrogen. (Preparation, *Berichte*, 22, 831.) It melts at 16° and boils at 230°. When oxidized, it yields metanitro-benzoic acid; when reduced, metatoluidine.

Ordinary *α*-**Dinitro-toluene**, $C_6H_3(NO_2)_2.CH_3$ (1, 2, 4—CH_3 occupying 1), is obtained from toluene, and from (1, 4)- and (1, 2)-nitrotoluene on boiling with fuming nitric acid (together with *m*-nitrotoluene, *Berichte*, 18, 1336). It crystallizes in long needles, melts at 71° and boils near 300°. It can be oxidized to dinitro-benzoic acid, from which we obtain (1, 3)-dinitro-benzene. Ammonium sulphide reduces the NO_2-group (in 4), and forms amido-nitrotoluene. Symmetrical dinitrotoluene (1, 3, 5) is formed from dinitro-paratoluidine, and melts at 92°.

Trinitro-toluene, $C_6H_2(NO_2)_3.CH_3$ (1, 2, 4, 6—CH_3 occupying 1), is prepared by heating toluene with nitric and sulphuric acids. It melts at 82°, and is oxidized with difficulty. It forms molecular compounds with benzenes and anilines (p. 588), and yields symmetrical trinitrobenzene when heated with nitric acid. The nitro-derivatives of the higher hydrocarbons have been mentioned with the latter.

NITROSO-COMPOUNDS.

Nitroso-benzene and nitroso-naphthalene are the only known derivatives in which the nitroso-group occupies the position of benzene-hydrogen. The so-called nitroso-phenols (see these), according to latest researches, possess a very different constitution, although they give the nitroso-reaction (p. 107).

Nitroso-benzene, $C_6H_5.NO$, is produced by the action of NOCl or NOBr upon a solution of mercury diphenyl, $(C_6H_5)_2Hg$, in benzene or carbon disulphide, or by letting nitrous acid act upon diphenyl tin chloride, $(C_6H_5)_2SnCl_2$. It is only known in solution, and has a sharp odor and green color. Tin and hydrochloric acid reduce it to aniline:—

$$C_6H_5NO + 2H_2 = C_6H_5.NH_2 + H_2O.$$

When digested with aniline acetate, azobenzene is formed:—

$$C_6H_5.NO + NH_2.C_6H_5 = C_6H_5.N:N.C_6H_5 + H_2O.$$

By oxidizing quinodioxime with alkaline potassium ferricyanide, there results a compound, which is very probably *Dinitrosobenzene*, $C_6H_4(NO)_2$ (1, 4). It has a golden yellow color, is insoluble in nearly all solvents and, when heated, sublimes with partial decomposition. Upon oxidation with HNO_3, it yields *p*-dinitrobenzene, and when reduced, *p*-phenylenediamine. When boiled with HCl-hydroxylamine it is reconverted into quinodioxime, $C_6H_4(N.OH)_2$ (*Berichte*, **20**, 615).

p **Dinitroso-toluene,** $C_6H_3(NO)_2.CH_3$, from toluquinone-dioxime, closely resembles the benzene derivative. It has an odor somewhat like ClOH. It detonates when heated to 144° (*Berichte*, **21**, 734).

AMIDO-COMPOUNDS.

These are produced by the substitution of amido-groups for the hydrogen of benzene:—

$C_6H_5NH_2$	$C_6H_4(NH_2)_2$	$C_6H_3(NH_2)_3$.
Amidobenzene.	Diamido-benzene.	Triamido-benzene.

Or, they may be considered as ammonia derivatives, from which might be concluded the existence of primary, secondary and tertiary amines of the benzene series (p. 157):—

$C_6H_5.NH_2$	$(C_6H_5)_2NH$	$(C_6H_5)_3N$.
Phenylamine.	Diphenylamine.	Triphenylamine.

The true analogues, *e.g.*, $C_6H_5.CH_2.NH_2$, of amines of the fatty series are obtained when the hydrogen of the side-chains is replaced by the amido-group. They are considered later.

The amido-compounds of the benzene series are prepared almost exclusively by the reduction of nitro-derivatives. The most important methods of reduction are:—

(1) The action of ammonium sulphide in alcoholic solution (Zinin in 1842):—

$$C_6H_5.NO_2 + 3H_2S = C_6H_5.NH_2 + 2H_2O + 3S.$$

The nitro-compound is dissolved in alcohol, concentrated ammonia added and hydrogen sulphide conducted into the hot mixture as long as sulphur is precipitated. Filter and concentrate the filtrate. In using this reaction with the di- and tri-nitro-compounds only one nitro-group is reduced at first, and in this manner it is therefore easy to obtain intermediate products, like the nitroamido-compounds. It is only by continued heating that the second nitro-group is reduced.

In the case of chlor-nitro-benzenes the nitro-group is only reduced by ammonium sulphide when it is not *adjacent* to the chlorine or another nitro-group; in the reverse instance sulphur will replace the chlorine or a nitro-group (*Berichte*, 11, 2056 and 1156).

(2) Action of zinc and hydrochloric acid upon the alcoholic solution of nitro-compounds (Hofmann); or iron filings and acetic or hydrochloric acid (Béchamp). The latter method is applied technically in the manufacture of aniline or toluidine; the reduction is accomplished by the nascent hydrogen and the resulting ferrous oxide:—

$$C_6H_5.NO_2 + 6FeO + H_2O = C_6H_5.NH_2 + 3Fe_2O_3.$$

(3) Action of tin and hydrochloric acid (or acetic acid) (Roussin):—

$$C_6H_5.NO_2 + 3Sn + 6HCl = C_6H_5.NH_2 + 3SnCl_2 + 2H_2O.$$

Stannous chloride reacts similarly:—

$$C_6H_5.NO_2 + 3SnCl_2 + 6HCl = C_6H_5.NH_2 + 3SnCl_4 + 2H_2O.$$

This method serves also for the quantitative determination of the nitro-groups (*Berichte*, 11, 35 and 40).

Pour fuming hydrochloric acid over the nitro-compound and gradually add the calculated quantity of granulated tin (1½ Sn for $1NO_2$); after a little time, usually without heating, a violent reaction ensues, and the tin and nitro-derivative both dissolve. The solution contains a double salt, *e. g.*, $(C_6H_5.NH_2.HCl)_2SnCl_4$, formed by the HCl-salt of the amide combining with tin chloride. These salts generally crystallize well. The tin is precipitated from the hot solution by hydrogen sulphide, the sulphide is filtered off and the filtrate contains the hydrochloride salt of the amido-compound. Alkalies will set the latter free. Sometimes in using tin and hydrochloric acid chlorinated amido-compounds are produced, therefore, in such cases it is advisable to substitute acetic acid. (*Berichte*, 20, 1567).

In this procedure, which is principally employed in laboratories, all the nitro-groups present in a compound are simultaneously reduced. The reduction can, however, be limited to single groups (Kekulé), if we apply an alcoholic HCl solution and take only half the tin requisite for complete reduction; thus, nitraniline results from dinitrobenzene. Partial reduction can also be effected by the action of the calculated quantity of stannous chloride in alcoholic solution (*Berichte*, 19, 2161).

Other reducing agents, finding occasional application, are: sodium arsenite, zinc dust (in alcoholic or ammoniacal solutions), tin and acetic acid (*Berichte*, 15, 2105), and HI and phosphorus iodide. Sodium amalgam, on the other hand, reduces nitro- to azo-compounds. A procedure, very well adapted for unsaturated nitro-compounds, consists in the use of ferrous sulphate and baryta-water or ammonia (*Berichte*, 15, 2299).

Only traces of amido-derivatives can be had by heating the haloid compounds, *e. g.*, C_6H_5Br, with ammonia; the same may be remarked of the phenols. Both classes of compounds, however, react more readily providing nitro-groups exist in the benzene nucleus. Thus, when (1, 2)- and (1, 4)-chlor- and brom-nitrobenzenes are heated with alcoholic ammonia, the corresponding nitranilines are produced, whereas the meta-compounds do not react (p. 588).

Amido-derivatives are similarly formed from the nitranisoles (alkylized phenols), when heated with aqueous or alcoholic ammonia to 180–200° (*Berichte*, 21 1541):

$$C_6H_4(NO_2).O.CH_3 + NH_3 = C_6H_4(NO_2).NH_2 + CH_3.OH.$$

Here again it is the para- and ortho-compounds which react, not the meta-variety.

The halogen atoms and oxyalkyls are more reactive in the presence of two or three nitro-groups. Thus α-chlor- and brom-dinitrobenzene yield dinitraniline (p. 588); dinitroanilines are formed from the α- and β-dinitrophenols (their ethers) (*Annalen*, 174, 276; *Berichte*, 21, 1541):—

$$C_6H_3(NO_2)_2.O.CH_3 + NH_3 = C_6H_3(NO_2)_2.NH_2 + CH_3.OH;$$

and chrysanisic acid is obtained from dinitroanisic acid.

In a few ortho-dinitro-compounds ammonia (also aniline) can replace a nitro-group by NH_2 (Laubenheimer), thus ortho-dinitrobenzene yields ortho-nitraniline, β-dinitrochlorbenzene yields nitroamido-chlorbenzene (p. 587). The phenols can also be directly transformed into amido-benzenes by heating them to 300° with ammonia-zinc chloride ($ZnCl_2.NH_3$), especially in the presence of ammonium chloride (*Berichte*, 19, 2916; 20, 1254): $C_6H_5.OH + NH_3 = C_6H_5.NH_2 + H_2O$. About 70 per cent. of amines are obtained by this method. The naphthols react even more readily. The divalent phenols react in like manner with aniline (*Berichte*, 16, 2812; 17, 2635).

The *secondary* and *tertiary* phenylamines cannot be prepared from the primary, *e.g.*, $C_6H_5.NH_2$, by action of C_6H_5Cl or C_6H_5Br. The secondary are obtained by heating the anilines with HCl-anilines (like the secondary acid amides) (p. 255):—

$$C_6H_5.NH_2.HCl + C_6H_5.NH_2 = (C_6H_5)_2NH + NH_3.HCl.$$

The tertiary phenylamines are prepared by treating the potassium compounds, $C_6H_5.NK_2$ or $(C_6H_5)_2NK$, with C_6H_5Br:—

$$C_6H_5.NK_2 + 2C_6H_5Br = (C_6H_5)_3N + 2KBr.$$

The amido-derivatives of the benzene hydrocarbons are organic bases: they combine with acids to form salts, just as the amines do, and are freed again by alkalies. But they are far more feeble bases than the alkylamines, because the phenyl group possesses a more negative character (p. 557). They do not show an alkaline reaction. The secondary phenylamines, *e.g.*, $(C_6H_5)_2NH$, are even less basic; their salts are decomposed by water, and tertiary triphenylamine is not capable of producing salts.

When negative groups enter the primary phenylamines, they further diminish their basic character; the salts of substituted anilines, like $C_6H_3Cl_2.NH_2$ and $C_6H_3(NO_2)_2.NH_2$, are decomposed by water, or are not produced.

The behavior of the phenylamines towards nitrous acid is very characteristic; it is perfectly analogous to that of the alkylamines (p. 157). The primary phenylamines exchange the group NH_2 for OH, and form phenols:—

$$C_6H_5.NH_2 + NO_2H = C_6H_5.OH + N_2 + H_2O.$$

Diazo-compounds and diazoamido-derivatives (see these) are intermediate products. The secondary phenylamines, *e. g.*, $(C_6H_5)_2NH$ and $C_6H_5.NH.CH_3$, yield *nitrosoamines* (p. 164):—

$$(C_6H_5)_2NH + NO.OH = (C_6H_5)_2N.NO + H_2O;$$

while from tertiary amido-derivatives we get the nitroso-products of the benzene nucleus:—

$$C_6H_5.N(CH_3)_2 \text{ yields } C_6H_4(NO).N(CH_3)_2.$$

Only the primary phenylamines are adapted to the formation ot carbylamines and mustard oils (pp. 287 and 279). Furfurol combines with all the amido-benzene derivatives, forming intense red-colored compounds.

On boiling the anilines with hydrochloric acid and concentrated nitric acid the amido-group is displaced and chlorbenzenes (together with chlorphenols) are produced. With HBr or HI and nitric acid the products are bromine and iodine derivatives (*Berichte*, **18**, 39).

On heating the HCl-salts of methyl and dimethyl aniline to 300°, the methyl group is transposed, and we get toluidine, xylidine, etc. (p. 580).

$C_6H_5.N(CH_3)_2$ yields $C_6H_4(CH_3).NH.CH_3$ and $C_6H_3(CH_3)_2.NH_2$.

A similar alkylizing of the benzene nucleus occurs on heating the HCl-anilines with alcohols to 300°, or the anilines with alcohols and $ZnCl_2$ to 280° (*Berichte*, 16, 105; 18, 132).

Aniline, $C_6H_5.NH_2$
Toluidine, $C_7H_7.NH_2$
Xylidine, $C_8H_9.NH_2$
Cumidine, $C_9H_{11}.NH_2$.

Aniline, $C_6H_5.NH_2$, amidobenzene, was first noticed by Unverdorben in 1826, in the dry distillation of indigo (crystallin), and later by Fritsche in the distillation of indigo with caustic potash (*Anilin*, 1841). Runge discovered (1834) it in coal-tar, and called it *cyanole*. Zinin was the first to prepare it artificially (1841), by reducing nitrobenzene with ammonium sulphide. It is formed in the dry distillation of many nitrogenous substances, for example, bituminous coal, bones, indigo and isatin. At present it is exclusively made by reducing nitrobenzene.

In the preparation of aniline on a large scale, nitrobenzene is heated with iron filings and hydrochloric acid (p. 592). The product of the reaction is mixed with lime and distilled with superheated steam. In a small way the reduction is best executed with tin and hydrochloric acid.

Aniline is a colorless liquid with a faint, peculiar odor, and boils at 183° (corr.); its specific gravity at 0° is 1.036. When perfectly pure it solidifies on cooling, and melts at —8°. It is slightly soluble in water (1 part in 31 parts at 12°) but dissolves readily in alcohol and ether. It shows a neutral reaction with litmus. When heated it expels ammonia from its salts, while in the cold ammonia separates it from its salts. Exposed to air aniline gradually assumes a brown color, and resinifies. Bleaching lime imparts a purple color to the solution. When a pine shaving is moistened with aniline salts it becomes yellow in color. On adding sulphuric acid and a few drops of potassium chromate to aniline, a red color appears; later it becomes an intense blue.

As a base aniline unites directly with acids, and also with some salts—$(C_6H_7N)_2.SnCl_2$, $(C_6H_7N)_2.CuSO_4$. Its salts crystallize well, and dissolve readily in water. The HCl-salt, $C_6H_7N.HCl$, forms deliquescent needles; platinic chloride precipitates a yellow-colored double salt, $(C_6H_7N.HCl)_2.PtCl_4$, from the alcoholic solution. The *nitrate*, $C_6H_7N.NO_3H$, crystallizes in large rhombic plates; the *oxalate*, $(C_6H_7N)_2.C_2O_4H_2$, obtained by mixing the alcoholic solutions, forms rhombic prisms.

On warming aniline with potassium, the hydrogen of the amido-group is replaced with formation of the compounds $C_6H_5.NHK$ and $C_6H_5.NK_2$: sodium does not react until heated to 200°. It acts more readily providing one hydrogen atom of the amido-group is substituted by acid radicals (as in acetanilide, $C_6H_5.NH.C_2H_3O$), or if halogen atoms be present in the benzene nucleus; in this case the halogen is reduced by the nascent hydrogen. The sodium compounds are oxidized to azo-compounds, when they are exposed to the air.

ANILINE SUBSTITUTION PRODUCTS.

These are obtained: (1) By the direct substitution of aniline. The anilines, like the phenols, are more susceptible of substitution than the benzenes. The action of the halogens is so energetic that the reaction requires to be moderated. When chlorine or bromine water acts upon the aqueous solution of aniline salts, their hydrogen atoms are directly substituted. Nitric acid converts aniline into nitrophenols. To get the mono- and di-substitution products, it is necessary to employ as points of departure the acid anilides, *e. g.*, acetanilide, $C_6H_5.NH.C_2H_3O$; these are first substituted, and the substituted anilines separated from them by boiling with alkalies or hydrochloric acid, or with sulphuric acid.

On allowing chlorine and bromine (in aqueous solution, or in vapor form) to act upon acetanilide suspended in water, only para-compounds are produced (p. 589), because the ortho-derivatives formed at the same time immediately pass into dihalogen derivatives. In the nitration of acetanilide mono-derivatives of the para-, ortho- and meta-series are formed. By nitration in presence of much sulphuric acid, meta-nitro-derivatives predominate (p. 589).

The union of the amid-group and the transposition into an acid group occur simultaneously (giving rise to a meta-substitution product, p. 589). Chlorine and bromine react in the same way with aniline and toluidine in the presence of concentrated sulphuric acid or hydrochloric acid (*Berichte*, 22, 2539 and 2903; 23, 1643).

When ortho- and para-substituted anilines are chlorinated, they almost invariably furnish tri-substituted products (1, 2, 4, 6), whereas the meta-series yield tetra- and penta-substitution products (*Berichte*, 15, 1328).

Iodine is capable of directly substituting the anilines, as the resulting hydriodic acid is taken up by the excess of aniline:—

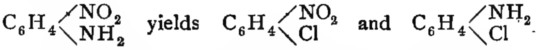
$$2C_6H_6.NH_2 + I_2 = C_6H_4I.NH_2 + C_6H_6.NH_2.HI.$$

(2) By the reduction of halogen nitrobenzenes by means of tin and hydrochloric acid, or ammonium sulphide (p. 592); thus, the three $C_6H_4Br.NO_2$ yield the corresponding $C_6H_4Br.NH_2$.

(3) The nitranilines can be prepared by heating haloid nitrobenzenes to 150–180° with alcoholic ammonia; or by heating the ethers of the nitrophenols, *e. g.*, $C_6H_4(NO_2).O.C_2H_5$, with aqueous

ammonia. In both instances the para- and ortho-compounds, and not the meta-, react (p. 589).

(4) The halogen anilines can be obtained from the nitro-anilines by first replacing the amido-group by halogens. This is accomplished through the diazo-compounds. The next step is, then, to reduce the nitro-group :—



$$C_6H_4{<}\begin{matrix}NO_2\\NH_2\end{matrix} \text{ yields } C_6H_4{<}\begin{matrix}NO_2\\Cl\end{matrix} \text{ and } C_6H_4{<}\begin{matrix}NH_2\\Cl\end{matrix}.$$

The ortho-compounds are weaker bases than the para- and meta-.

Ortho- and Meta-chloraniline, from the corresponding chlornitro benzenes, are liquids; the first boils at 207°; its specific gravity at 0° is 1.23; the second boils at 230°; its specific gravity at 0° is 1.24. **Parachloraniline**, formed from (1, 4)-nitraniline and nitrochlorbenzene, and by the chlorination of acetanilide, crystallizes in shining, rhombic octahedra, which are somewhat soluble in hot water. It melts at 70–71° and boils at 230–231°, with scarcely any decomposition. The HCl-salt is slightly soluble in cold water.

Ortho-bromaniline, $C_6H_4Br.NH_2$, from *o*-($Br.NO_2$) and *o*-($NH_2.NO_2$), crystallizes in needles, melting at 31.5° and boiling at 229°. **Metabromaniline**, from *m*-nitroaniline and *m*-bromnitrobenzene, melts at 18° and boils at 251°. **Parabromaniline**, from *p*-nitraniline and *p*-nitrobrombenzene, is easily obtained by conducting bromine vapor into acetanilide. It crystallizes in shining, rhombic octahedra, and melts at 63° (66°). The action of sodium upon the ethereal solution produces benzidine. When distilled it breaks up into aniline, *α*-dibromaniline and *α*-tribromaniline.

Ortho-iodoaniline, $C_6H_4I.NH_2$, prepared by the reduction of *o*-nitroiodobenzene, melts at 56.5°. It is very volatile (*Berichte*, 21, Ref. 348). **Metaiodoaniline**, from *m*-nitraniline, forms silvery laminæ, and melts at 27°. **Paraiodoaniline** is formed from *p*-nitroiodobenzene and by the direct action of iodine upon aniline, or by the action of chlor-iodine upon acetanilide. It consists of needles or prisms, melting at 63°, and somewhat soluble in hot water. With ethyl iodide it yields ethyl-aniline: $C_6H_4I.NH_2 + C_2H_5I = C_6H_5.NH.C_2H_5 + I_2$.

α-**Dichloraniline**, $C_6H_3Cl_2.NH_2$, from dichloracetanilide (1, 2, 4—NH_2 in 1), crystallizes in needles, and melts at 63°. *β*-**Dichloraniline**, from nitro- (1, 4)-dichlorbenzene (p. 581), melts at 54° (*Annalen*, 196, 215).

α-**Dibromaniline**, $C_6H_3Br_2.NH_2$ (1, 2, 4—NH_2 in 1), is obtained from dibromacetanilide and from nitro-(1, 3)-dibrombenzene (melting at 61°, p. 582); it melts at 79°. *β*-**Dibromaniline**, from nitro-(1, 4)-dibrombenzene, melts at 51–52°.

α-**Trichloraniline**, $C_6H_2Cl_3.NH_2$ (chlorine in 1, 3, 5), is formed by conducting chlorine into the aqueous solution of HCl·aniline. It melts at 77.5° and boils at 260°. It no longer combines with acids. Symmetrical trichlorbenzene is obtained from it by substituting H for NH_2. *β*-**Trichloraniline**, (1, 2, 4, 5 — NH_2 in 1), from nitro-(1, 2, 4)-trichlorbenzene, melts at 96.5° and boils at 270°.

α-**Tribromaniline**, $C_6H_2Br_3.NH_2$ (bromine in 1, 3, 5), is formed on conducting bromine vapors into aqueous HCl-aniline; it crystallizes in long needles, melts at 119°, and forms salts with difficulty (*Berichte*, 16, 635). It yields symmetrical tribrombenzene. *β*-**Tribromaniline** (1, 2, 4, 5 — NH_2 in 1) is obtained from ordinary tribrombenzene (1, 2, 4) by nitration and reduction, and does not melt, even at 130°.

Nitranilines, $C_6H_4(NO_2).NH_2$:—

		(1, 2)	(1, 3)	(1, 4)
$C_6H_4\left\{\begin{matrix}NH_2\\NO_2\end{matrix}\right.$	M. P.	71°	114°	147°
$C_6H_4\left\{\begin{matrix}NH_2\\NH_2\end{matrix}\right.$	"	102°	63°	147°
$C_6H_4\left\{\begin{matrix}NO_2\\NO_2\end{matrix}\right.$	"	118°	90°	172°.

The three nitranilines can be obtained from the three corresponding dinitrobenzenes, by incomplete reduction with ammonium sulphide (p. 592). Ortho- and para- nitranilines are also produced from the corresponding haloid nitrobenzenes, the ethers of nitrophenols and dinitro-benzenes, upon heating with ammonia (p. 588); also by the nitration of acetaniline. The easiest course to pursue in making the three compounds, is to dissolve aniline-sulphate in an excess of concentrated sulphuric acid, and add the calculated amount of fuming nitric acid. Precipitate with water and distil in a current of steam, when the ortho- and the meta-products pass over, while the para remains. The para and meta occur rather abundantly, the ortho only in small amount (*Berichte*, 10, 1716; 17, 261).

Ortho-nitraniline (1, 2), is most easily obtained by heating *o*-nitranilinesulphonic acid (from acetyl anilinesulphonic acid) with hydrochloric acid to 170° (*Berichte*, 18, 294), or by the action of ammonia upon *o*-nitrophenol at 160° (*Berichte*, 19, 1749). It forms yellow needles, melting at 71°; it dissolves in water and alcohol more readily than its isomerides, and is more reactive. It yields (1, 2)-diamido-benzene when reduced.

Metanitraniline (1, 3) consists of long yellow needles, melting at 114°. Water decomposes its salts. By reduction it yields (1, 3)-diamido-benzene. Para-nitraniline (1, 4) forms yellow needles or plates, melts at 147°, and yields (1, 4)-diamido-benzene.

Of all the HCl-salts of the nitranilines that of *o*-nitraniline is most easily decomposed by water, then follows *p*-nitraniline, while the salt of metanitraniline is the most stable. From this it is evident that the basicity of the nitranilines successively diminishes in the order: meta-, para-, ortho (*Berichte*, 17, 2719). The same is observed in the deportment of the aceto-nitranilines with alkalies (*Berichte*, 19, 337).

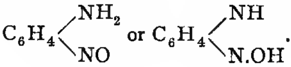
When ortho- and para-nitranilines (not meta) are boiled with alkalies, they part with NH_3, and are converted into their corresponding nitrophenols, $C_6H_4(NO_2).OH$; the di- and tri-nitranilines react even more readily.

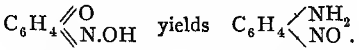
Dinitranilines, $C_6H_3(NO_2)_2.NH_2$. The so-called *a-dinitraniline* is obtained from dinitrochlor- and dinitrobrom-benzene, also from *a*-dinitrophenol (its ether), when they are treated with ammonia in the heat. It melts at 182°, and by elimination of the NH_2 yields ordinary dinitro-benzene (1, 3). Hence, its structure is (1, 2, 4—NH_2 in 1).

β-Dinitraniline is obtained from *β*-dinitrophenol. It melts at 138°, and also yields (1, 3)-dinitro-benzene, hence its structure is (1, 2, 6—with NH_2 in 1).

Trinitraniline, $C_6H_2(NO_2)_3.NH_2$, called Picramide, is obtained from picric acid through its ether, or by means of picryl chloride (p. 590). The latter reacts with ammonia, even in the cold. It forms orange-red needles, and melts at 186°. Its structure is analogous to that of picric acid (1, 2, 4, 6—NH_2 in 1). It forms picric acid when heated with alkalies:—

$$C_6H_2(NO_2)_3.NH_2 + KOH = C_6H_2(NO_2)_3.OK + NH_3.$$

Nitroso-anilines,  $C_6H_4\left\langle\begin{matrix}NH_2\\NO\end{matrix}\right.$ or $C_6H_4\left\langle\begin{matrix}NH\\N.OH\end{matrix}\right.$. These compounds are produced when the nitrophenols or quinoximes are heated with ammonium chloride and ammonium acetate (*Berichte*, 20, 2474; 21, 684):—



$$C_6H_4\left\langle\begin{matrix}O\\ N.OH\end{matrix}\right. \text{ yields } C_6H_4\left\langle\begin{matrix}NH_2\\ NO\end{matrix}\right. .$$

Quinoxime. Nitrosoaniline.

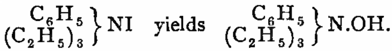
The nitroso-toluidines are similarly obtained from nitrosocresols (*Berichte*, 21, 729).

p-**Nitroso-aniline**, $C_6H_4(NO)(NH_2)$, crystallizes in steel-blue needles, melting at 174°. Its solutions (in benzene, water) show a bright green color. It dissolves in sodium hydroxide, forming a sodium salt. When boiled with this reagent it is again resolved into ammonia and nitrosophenol. HCl-Hydroxylamine converts it into quino-dioxime, $C_6H_4(N.OH)_2$. Phenylhydrazine changes it to *p*-phenylenediamine and a nitroso-diazo compound (*Berichte*, 22, 623).

ALCOHOLIC ANILIDES.

We find that, as in the amines of the fatty series, so in aniline, the hydrogen of the amido-group can be replaced by alcohol and acid radicals. The alkyl derivatives are formed in the same manner as the amines of the paraffin series (p. 157), by the action of the alkyl bromides and iodides upon aniline. This occurs mostly at ordinary temperatures. They can be directly produced by heating HCl-anilines with the alcohols to 250°. Alkyl chlorides are first produced, but they subsequently act upon aniline. The alkylization is more easily effected by using the HBr-salts (*Berichte*, 19, 1939).

The tertiary derivatives, *e. g.*, $C_6H_5.N(C_2H_5)_2$, combine further with the alkylogens, forming ammonium compounds, which moist silver oxide or lime converts into ammonium hydroxides:—



$$\left.\begin{matrix}C_6H_5\\ (C_2H_5)_3\end{matrix}\right\}NI \text{ yields } \left.\begin{matrix}C_6H_5\\ (C_2H_5)_3\end{matrix}\right\}N.OH.$$

The alkylic anilines can, *vice versa*, be re-formed. Dimethyl aniline results when the ammonium hydrate or its haloid salts are distilled. This product, by further heating with HCl or HI to 150°, or by the distillation of its hydrochloride, regenerates methyl-aniline and aniline (p. 160). When dimethyl aniline hydrochloride is heated to 250–300°, a rearrangement occurs, the alkyls enter the benzene nucleus, first in the para-position (4), then the ortho-positions (1) and (6). *p*-Toluidine, metaxylidine and finally mesidine are produced. *o*-Toluidine deports itself similarly (*Berichte*, 21, 640). When acetyl chloride acts upon the dialkyl anilines the alkyl-groups split off quite easily (*Berichte*, 19, 1947).

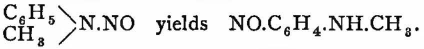
The aniline salts form ferrocyanogen salts with potassium ferrocyanide; these serve to separate the anilines (*Annalen*, 190, 184).

The methylated anilines are technically applied in the production of aniline dye-stuffs. They are formed on heating aniline together with HCl-aniline and methyl alcohol to 220°. A better course is to conduct CH_3Cl into boiling aniline. Methyl and di-methyl aniline occur in both instances, together with unaltered aniline. Consult *Berichte*, 10, 795, 22, 1005, for their separation and detection.

Methyl Aniline, $C_6H_5.NH(CH_3)$, , is obtained pure from its nitroso-compound by reduction with tin and hydrochloric acid, or by the saponification of the acetyl derivative. The latter can be prepared from the sodium acetanilide, $C_6H_5.N(Na).C_2H_3O$, by treatment with methyl iodide (*Berichte*, 17, 267). It boils at 190–191°, has an odor resembling that of aniline and a specific gravity at 15° of 0.976. Its salts (with HCl and H_2SO_4) do not crystallize and dissolve in ether. Hence, dilute sulphuric acid in ethereal solution does not separate methyl aniline in crystalline form, as it does with aniline. Bleaching lime imparts no color to it. With acetyl chloride or acetic anhydride, it forms the crystalline *acetyl derivative*, $C_6H_5.N(CH_3).C_2H_3O$, which melts at 101°, and boils at 245°. When methyl aniline is heated to 330°, it is transformed into paratoluidine, $C_6H_4(CH_3).NH_2$.

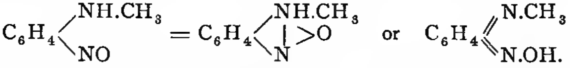
Nitroso-methyl-aniline, $\left.\begin{array}{l}C_6H_5\\CH_3\end{array}\right\}N.NO$, Phenyl methyl-nitrosamine (p. 594), is produced by the action of nitrous acid upon methyl aniline (also other secondary phenylamines), or better by KNO_2 upon the solution of its HCl-salt. It separates as a brown oil, which can be extracted with ether (*Berichte*, 19, 2123 and 18, 1997; *Annalen*, 190, 151). When distilled with steam it yields a yellow, aromatic-smelling oil, that solidifies in the cold, and melts at 12–15°. It cannot be distilled alone. It shows the nitroso reaction (p. 107) and does not combine with acids. HgNa, or zinc dust and acetic acid reduce it to methyl phenyl hydrazine. It regenerates methyl aniline with zinc and sulphuric acid, tin and hydrochloric acid, or by gently heating with $SnCl_2$. Reaction with anilines or an alcoholic potash solution accomplishes the same (*Berichte*, 11, 757). See *Berichte*, 17, 2668 upon the action of the nitrosamines upon the anilines.

When acted on by alcoholic hydrochloric acid methyl-aniline-nitrosamine rearranges itself to *p*-**nitrosomethylaniline** (*Berichte*, 19, 2991; 21, Ref. 228):—



$$\left.\begin{array}{l}C_6H_5\\CH_3\end{array}\right>N.NO \quad \text{yields} \quad NO.C_6H_4.NH.CH_3.$$

p-**Nitrosomethylaniline,** $C_6H_4(NO).NH.CH_3$, is perfectly analogous to *p*-nitrosodimethylaniline (see below). Its HCl-salt is not very stable. The free base forms large crystals with metallic lustre and melts at 118° C. It is soluble in dilute sodium hydroxide, forming the sodium compound, $C_7H_8N_2O.NaOH$, from which it is again liberated by carbon dioxide. It therefore probably possesses a structure analogous to that of the nitrosophenols or quinoximes (*Berichte*, 20, 532, 1252):—



$$C_6H_4\left<\begin{array}{l}NH.CH_3\\NO\end{array}\right. = C_6H_4\left<\begin{array}{l}NH.CH_3\\ \,|\;>O\\N\end{array}\right. \quad \text{or} \quad C_6H_4\left<\!\!\!\left<\begin{array}{l}N.CH_3\\N.OH.\end{array}\right.\right.$$

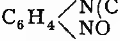
When heated with sodium hydroxide *p*-nitrosomethyl aniline is decomposed into *p*-nitrosophenol and methylaniline:—

$$C_6H_4(NO).NH.CH_3 + H_2O = C_6H_4(NO).OH + NH_2CH_3.$$

Methenyl amido-thiophenol and similar thiazole-like compounds are produced upon heating methyl and dimethyl aniline with sulphur (*Berichte*, 21, 60).

Dimethyl Aniline, $C_6H_5.N(CH_3)_2$, is obtained pure by distilling trimethyl-phenyl ammonium hydrate or its HCl-salt. The commercial article contains as much as 5 per cent. of methyl aniline. It is an oil boiling at 192° and solidifying at + 5°; its sp. gr. is 0.955. Its salts do not crystallize. It forms an acetate, $C_6H_5N(CH_3)_2.C_2H_4O_2$, with acetic acid; this decomposes again on distillation. Hypochlorites do not color it. It forms $C_6H_5.N(CH_3)_3I$ with methyl iodide.

Dimethyl aniline is remarkable because in it, as in the phenols, there is a reactive H-atom in the benzene nucleus. The action of nitrous acid, or better, sodium nitrite, upon the HCl-salt (*Berichte*, 12, 523) produces the HCl-salt of **p-Nitroso-dimethyl Aniline**,



$C_6H_4\begin{cases}N(CH_3)_2\\NO\end{cases}$

(*Berichte*, 20, 1252). This forms needles, which are not very soluble in water. The free base, separated from its salts by sodium carbonate, crystallizes in green, metallic-like laminæ, melting at 85°. It yields dyestuffs with phenols and anilines. $KMnO_4$ and ferricyanide of potassium oxidize it to nitro-dimethyl-aniline. Warm, dilute caustic soda decomposes it into dimethyl aniline and paranitroso-phenol (p. 600).

p-Nitro-dimethyl Aniline, $C_6H_4(NO_2).N(CH_3)_2$, is obtained in the oxidation of the nitroso-compound and by the action of fuming nitric acid (1 mol.) upon dimethyl aniline in glacial acetic acid (10 parts) solution; it melts at 162°. **Meta-nitro-dimethyl Aniline** is produced together with the para-compound. It forms salts with acids (*Berichte*, 19, 545). **Dinitro-dimethyl Aniline** (1, 2, 4), obtained by further nitration (see *Berichte*, 19, 2123; 18, 1997), is also formed from α-dinitrochlorbenzene (p. 588), and trimethylamine (*Berichte*, 15, 1234); it melts at 78° and is easily decomposed by potash into dimethyl aniline and α-dinitrophenol. Further nitration produces trinitrophenyl methylnitramine, $C_6H_2(NO_2)_3.N(CH_3).(NO_2)$ (*Berichte*, 22, Ref. 343).

p-Amido-dimethyl Aniline, $C_6H_4(NH_2).N(CH_3)_2$, dimethyl-paraphenylene diamine, is formed by the reduction of the nitroso- and nitro-compounds. It may be obtained by the decomposition of helianthine (*Berichte*, 16, 2235). It melts at 41° and boils at 257°. In acid solution it gives a dark blue coloration (methylene blue) with hydrogen sulphide and ferric chloride, and answers as a sensitive reagent for hydrogen sulphide.

Other groups can replace a benzene hydrogen in dimethyl aniline. For example, an acid chloride (of dimethyl amido-benzoic acid) and ketones are produced by the action of $COCl_2$. Benzoyl chloride (see *Berichte*, 18, 685), benzyl chloride and chloroxalic ester react similarly, whereas by the action of chlor- or iod-acetic acids or their esters a methyl group is displaced and phenylglycocoll results (*Berichte*, 17, 2661):—

$$C_6H_5.N(CH_3)_2 + CH_2I.CO_2H = C_6H_5.N(CH_3).CH_2.CO_2H + CH_3I.$$

A methyl group is similarly split off by acetyl chloride or benzyl chloride (p. 599).

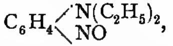
Dimethyl aniline, like the phenols, forms condensation products with aldehydes (oil of almonds, furfurol, chloral, etc.); it combines with chlorides to yield phthaleïnes and green dyestuffs, and with benzotrichloride, $C_6H_5.CCl_3$, to form the so-called *malachite green*. A condensation of several benzene groups takes place, with the production of compounds which are allied to triphenyl methane and the aniline colors.

Dimethyl aniline and chloral condense to  $C_6H_4\left\langle\begin{matrix}N(CH_3)_2\\CH(OH).CCl_3\end{matrix}\right.$, which yields  $C_6H_4\left\langle\begin{matrix}N(CH_3)_2\\CHO\end{matrix}\right.$ with alkalies (*Berichte*, 19, 365).

The so-called **Azylines** are tetra-alkyl-para-diamido-azobenzenes (see these): $R_2N.C_6H_4.N_2.C_6H_4.NR_2$. They are formed when nitric oxide acts upon the tertiary anilines. Nitric acid converts the dialkyl anilines into **nitramines**, *e. g.*, tri-nitrophenylnitramine, $C_6H_2(NO_2)_3.N(CH_3)(NO_2)$ (p. 164).

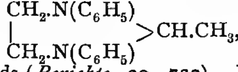
Ethyl Aniline, $C_6H_5.NH.C_2H_5$, boils at 204°; its specific gravity at 18° is 0.954. Its *nitrosamine derivative*, $C_6H_5.N(NO).C_2H_5$, is a yellow oil, with an odor resembling that of bitter almonds; it does not unite with acids and cannot be distilled (*Berichte*, 8, 1641). Alcoholic hydrochloric acid converts it into ***p*-Nitroso-Ethyl Aniline,** $C_6H_4(NO).NH.C_6H_5$, which crystallizes in green leaflets, melting at 78°.

Methyl Ethyl Aniline, $C_6H_5.N(CH_3).(C_2H_5)$, boils at 201°. Its compound with CH_3I is identical with dimethyl-aniline-ethyl iodide; methyl-ethyl aniline-ethyl iodide is also identical with diethyl aniline-methyl-iodide—an additional proof that *the five affinities of nitrogen have equal value* (p. 166 and *Berichte*, 19, 2785). Ethyl iodide is set free from all these ammonium iodides when they are heated with caustic potash.

Diethyl Aniline, $C_6H_5.N(C_2H_5)_2$, boils at 213°; its specific gravity at 18° is 0.939. When heated with ethyl iodide it forms $C_6H_5.N(C_2H_5)_3I$, from which silver oxide separates the strong ammonium base, $C_6H_5.N(C_2H_5)_3.OH$; the latter decomposes on distillation into diethyl aniline, ethylene and water. The *nitroso-compound*,  $C_6H_4\left\langle\begin{matrix}N(C_2H_5)_2\\NO\end{matrix}\right.$, forms large, green prisms, which melt at 84°, and yield nitroso-phenol and diethylamine, when boiled with dilute caustic soda.

Allyl Aniline, $C_6H_5.NH.C_3H_5$, from aniline and allyl iodide, boils at 208°; it yields quinoline, C_9H_7N, when distilled over heated lead oxide.

The derivatives with *divalent* alcohol radicals are formed the same as the alkyl anilines. **Methylene-diphenyl-diamine,** $(C_6H_5.NH)_2CH_2$, from aniline and methylene iodide, is a thick liquid. Aniline yields **methylene aniline,** $C_6H_5.N{:}CH_2$ (?), when acted upon by formic aldehyde. Bright crystals (*Berichte*, 18, 3309, Ref. 71).

Ethylene-diphenyl-diamine, $(C_6H_5.NH)_2C_2H_4$, from aniline and ethylene bromide, is crystalline, and melts at 65°. Ethylene aniline condenses with aldehydes, forming bases like  $\left.\begin{matrix}CH_2.N(C_6H_5)\\|\\CH_2.N(C_6H_5)\end{matrix}\right>CH.CH_3$, which are again resolved into their components by acids (*Berichte*, 20, 732). Isomeric **ethidene-diphenyl diamine,** $(C_6H_5.NH)_2.CH.CH_3$, is produced in the cold from aniline and aldehyde. It is amorphous. Similar compounds are produced with other aldehydes, *e.g.*, valeral, acroleïn and furfurol. With chloral it gives **Trichlorethidene-diphenylamine,** $(C_6H_5.NH)_2CH.CCl_3$, melting at 100°. **Acroleïn-aniline,** $C_6H_5.N{:}CH.CH{:}CH_2$ (?), is amorphous and yields quinoline, C_9H_7N, upon distillation.

Diethylene-diphenyl-diamine, $(C_6H_5.N)_2.(C_2H_4)_2$, or **Diphenyl Piperazine,**  $C_6H_5.N\left\langle\begin{array}{c}CH_2.CH_2\\CH_2.CH_2\end{array}\right\rangle N.C_6H_5$, a derivative of piperazine, $C_4H_{10}N_2$, is produced when aniline is heated with ethylene bromide and caustic potash, or sodium carbonate (*Berichte*, 22, 1387, 1778). It crystallizes from alcohol in needles melting at 163°.

PHENYLATED PHENYLAMINES (p. 594).

Diphenylamine, $(C_6H_5)_2NH$, is produced in the dry distillation of triphenyl rosaniline (Rosaniline blue), and is prepared by heating aniline hydrochloride and aniline to 240° :—

$$C_6H_5.NH_2.HCl + C_6H_5.NH_2 = (C_6H_5)_2NH + NH_4Cl.$$

It results also upon heating aniline with phenol and $ZnCl_2$ to 260°. It is a pleasant-smelling, crystalline compound, melting at 54°, and boiling at 310° (corrected). It is almost insoluble in water, but readily soluble in alcohol and ether. It is a very weak base, whose salts are decomposed by water. Nitric acid or sulphuric acid, containing nitrogen oxides, colors it a deep blue, and it serves in the preparation of various dye-stuffs. The *acridines* are obtained when diphenylamine is heated to 300° with fatty acids.

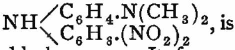
Methyl Diphenylamine $(C_6H_5)_2N.CH_3$, is formed by the action of methyl chloride upon diphenylamine. It boils at 290–295° (282°). **Diphenyl nitrosamine,** $(C_6H_5)_2N.NO$, is produced when ethyl nitrate acts on diphenylamine, or by the addition of HCl-diphenylamine to an acetic acid solution of potassium nitrite. Yellow plates of great brilliancy, melting at 66.5°. It dissolves with a deep blue color in concentrated sulphuric and hydrochloric acids. Alcoholic hydrochloric acid changes it to *p*-**Nitroso-diphenylamine,** $C_6H_5.NH.C_6H_4.NO$ (p. 600), crystallizing in green plates, which melt at 143°. It splits up into *p*-nitrosophenol, $C_6H_4(NO).OH$, and aniline when boiled with alkalies (*Berichte*, 20, 1252; 21, Ref. 227).

p-**Nitrodiphenylamine,** $C_6H_4(NO_2).NH.C_6H_5$, from benzoyl nitro-diphenylamine, forms reddish-yellow needles, melting at 132°. *o*-**Nitrodiphenylamine** results from aniline and *o*-chlornitrobenzene. It crystallizes in leaflets melting at 75° (*Berichte*, 22, 903). *p*-**Dinitrodiphenylamine,** $[C_6H_4(NO_2)]_2NH$, consists of yellow needles with a blue schimmer, and melts at 214°.

Various **Tri- and Tetranitro-diphenylamines** are produced by the action of chlor-dinitro- and trinitro-benzenes upon aniline and nitro-anilines. **Hexanitrodiphenylamine,** $[C_6H_2(NO_2)_3]_2NH$, is formed by the direct nitration of diphenylamine and methyl diphenylamine. Yellow prisms melting at 238° (*Berichte*, 19, 845). It dissolves with a purple-red color, in the alkalies, forming salts. Its ammonium salt occurs in commerce as a brick-red powder, bearing the name *Aurantia ;* it colors wool and silk a beautiful orange.

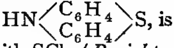
p-**Amido-diphenylamine,** $C_6H_5.NH.C_6H_4(NH_2)$, is formed by the reduction of its nitro- or nitroso-compound (*Berichte*, 23, Ref. 102), and also by the decomposition of phenylamido-azobenzene and diphenylamidoazobenzene sulphonic acid (tropæoline 00) (see azo-compounds). It consists of laminæ melting at 61°. *p*-**Diamido-diphenylamine,** $[C_6H_4(NH_2)]_2NH$, is obtained in the reduction of the dinitro-compound, and by the decomposition of aniline black, and the reduction of phenylene blue with zinc dust and alkali. It crystallizes from water in leaflets, melting at 158°. It forms quinone when oxidized; ferric chloride or chromic acid colors it dark green. Its **tetramethyl compound** is formed by the reduction of dimethyl phenylene green.

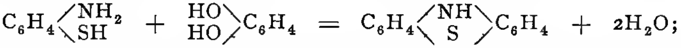
Diamido-diphenylamine bears a close relation to the indamine- and indoaniline dyestuffs (see these).

Dimethyl-amido-dinitro-diphenylamine,  $NH\Big\langle{C_6H_4.N(CH_3)_2 \atop C_6H_3.(NO_2)_2}$, is formed from *p*-amido-dimethyl aniline and *op*-dinitro-chlorbenzene. It forms bronze-colored leaflets (*Berichte*, 23, 2739).

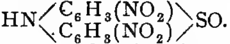
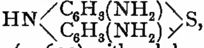
Oxy- and Dioxydiphenylamines are formed on heating anilines with dioxybenzenes (resorcin, hydroquinone) and $CaCl_2$ to 250–270°; at higher temperatures, and with $ZnCl_2$ we get diphenyl-phenylenediamines, $C_6H_4(NH.C_6H_5)_2$. (*Berichte*, 16, 2812). ***p*-Oxydiphenylamine,** from hydroquinone and aniline (*Berichte*, 17, 2431), melts at 70° and distils about 340°. When heated with sulphur it yields oxythiodiphenylamine (see below).

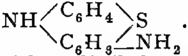
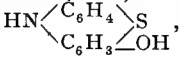
The oxydiphenylamines are closely allied to the indophenol dyestuffs.

Thiodiphenylamine,  $HN\Big\langle{C_6H_4 \atop C_6H_4}\Big\rangle S$, is produced on heating diphenylamine with sulphur to 250° or with SCl_2 (*Berichte*, 21, 2063). It crystallizes from alcohol in yellow laminæ, melts at 180°, and boils near 370°. A purely synthetic method for its preparation consists in heating *o*-amidothiophenol with pyrocatechol to 220°:—



$$C_6H_4\Big\langle{NH_2 \atop SH} + {HO \atop HO}\Big\rangle C_6H_4 = C_6H_4\Big\langle{NH \atop S}\Big\rangle C_6H_4 + 2H_2O;$$

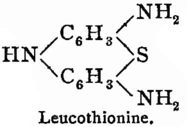
it follows from this that the two phenylene groups occupy the two ortho positions (*Berichte*, 19, 3255). It is neutral and does not combine with acids. Its imide hydrogen can be replaced by alkyls and acid radicals (*Berichte*, 18, 1844). Fuming nitric acid converts it into a **dinitro-sulphoxide,**  $HN\Big\langle{C_6H_3(NO_2) \atop C_6H_3(NO_2)}\Big\rangle SO$. Reduction changes this to **diamido-thio-diphenylamine,**  $HN\Big\langle{C_6H_3(NH_2) \atop C_6H_3(NH_2)}\Big\rangle S$, which is also produced by heating *p*-diamido-diphenylamine (p. 603) with sulphur (*Berichte*, 17, 2857). When this product is oxidized with ferric chloride, it yields *Lauth's violet*, which may be again reduced to the diamido-compound.

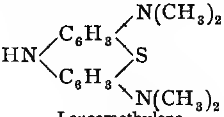
A moderated nitration of thiodiphenylamine produces **mononitrosulphoxide,** which is reduced to **amidothiodiphenylamine,**  $NH\Big\langle{C_6H_4 \atop C_6H_3\langle NH_2}\Big\rangle S$. When the latter is oxidized it yields a dyestuff like the violet. Similarly, ***p*-Oxydiphenylamine** (above), when heated with sulphur, forms an **Oxythiodiphenylamine,**  $HN\Big\langle{C_6H_4 \atop C_6H_3\langle OH}\Big\rangle S$, which may be oxidized to a dyestuff (*Berichte*, 17, 2860).

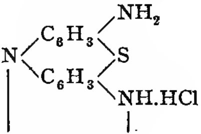
Triphenylamine, $(C_6H_5)_3N$, is obtained on heating dipotassium aniline (p. 594) or sodium diphenylamine with brombenzene (*Berichte*, 18, 2156). It crystallizes from ether in large plates, melts at 127°, and distils undecomposed. It dissolves in sulphuric acid, forming a violet, then a dark green color. It cannot form salts with acids. By nitration it yields a trinitro-product that forms *triamido-triphenylamine*, $N(C_6H_4.NH_2)_3$, by reduction (*Berichte*, 19, 759). Hexaphenyl-rosaniline is produced when phosgene acts upon triphenylamine.

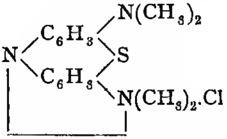
Diphenylamine Dyes.

Thiodiphenylamine is a *chromogen*, *i. e.*, a substance yielding colors, from which *leuco-compounds* of dyestuffs are obtained by the entrance of NH_2, NR_2 or OH (see rosaniline). When the leuco-derivatives are oxidized (split off 2H-atoms, while at the same time 2N-atoms are combined) *colors* are produced, the salts of which are the real dyes. These have been called Lauth's dyestuffs (Bernthsen, *Annalen*, **230**, 73; *Berichte*, **18**, Ref. 705; *Annalen* **251**, 1; *Berichte*, **22**, 390). The most important are:—


Leucothionine.


Leucomethylene Blue.

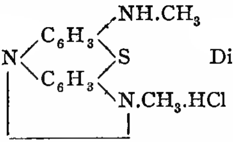

HCl-Thionine.
Lauth's Violet.


Tetramethyl Thionine-hydrochloride.
Methylene Blue.

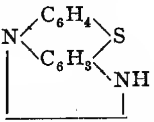
Lauth's violet (*thionine*) can be produced from thiodiphenylamine after the manner above described. An easier course is that adopted by Lauth, viz., to oxidize an H_2S-solution of *p*-phenylenediamine, $C_6H_4(NH_2)_2$, with ferric chloride. It is a direct color for silk and wool, but only attacks cotton after the latter has been mordanted. Owing to its high price it has not been used to any great extent.

Methylene blue, discovered by Caro in 1877, is more important. It is formed by oxidizing dimethyl-*p*-phenylenediamine, $H_2N.C_6H_4.N(CH_3)_2$, with $FeCl_3$ in the presence of H_2S. On adding sodium chloride and zinc chloride it is precipitated as the $ZnCl_2$-double salt. This is the methylene blue or *fast blue* found in commerce. It dyes silk with ease, and also mordanted cotton. It is the most stable cotton blue. By reduction it yields its leuco-base (the HCl-salt) $C_{16}H_{19}N_3S.HCl$-*tetramethyldiamido-thiodiphenylamine*. This reacts with methyl iodide, forming a methyl compound, which also results from diamido-thiodiphenylamine, and in this way proves the connection between methylene blue and Lauth's violet.

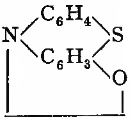
Dimethyl- and *diethyl thionine* (*Berichte*, **20**, 931) result from methyl- and ethyl-paraphenylenediamine by oxidation in the presence of H_2S:—


Dimethylthionine.

Oxidation of amidothiodiphenylamine and oxythiodiphenylamine (p. 604) produces the compounds—

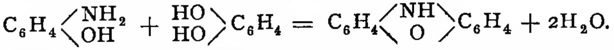

Imidothiodiphenylimide.

and


Oxythiodiphenylimide.

See *Annalen*, 230, 169 for additional analogous derivatives.

Phenazoxine, or phenoxazine, is a chromogen analogous to thiodiphenylamine. It is obtained by heating *o*-amidophenol with pyrocatechol:—



$$C_6H_4\left\langle\begin{matrix}NH_2\\OH\end{matrix}\right. + \left.\begin{matrix}HO\\HO\end{matrix}\right\rangle C_6H_4 = C_6H_4\left\langle\begin{matrix}NH\\O\end{matrix}\right\rangle C_6H_4 + 2H_2O.$$

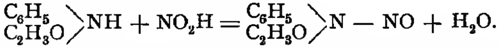
Its nitro product, when reduced, yields a leuco-amide compound, which forms a red-violet dye upon oxidation. *Methylene red* is a by-product in the preparation of methylene blue (*Annalen*, 251, 1; *Berichte*, 22, Ref. 390).

ACID ANILIDES.

An atom of hydrogen of the amido- or imid-group in the primary and secondary anilines, can also be replaced by acid radicals. The resulting compounds are termed *anilides*, and are formed according to methods similar to those used with the acid amides of the fatty series (p. 255); by the action of acid chlorides or acid anhydrides upon the anilines, or by heating the organic salts of the latter:—

$$\underset{\text{Aniline Acetate.}}{C_6H_5.NH_3.O.CO.CH_3} = \underset{\text{Acetanilide.}}{C_6H_5NH.CO.CH_3} + H_2O.$$

They are very stable derivatives; can usually be distilled without change, and also directly chlorinated, brominated and nitrated (p. 596). They are resolved into their components by digesting them with alkalies or heating with hydrochloric acid. The secondary anilides, like secondary alkylanilides (p. 594), yield *nitrosamines* by the action of nitrous acid:—



$$\left.\begin{matrix}C_6H_5\\C_2H_3O\end{matrix}\right\rangle NH + NO_2H = \left.\begin{matrix}C_6H_5\\C_2H_3O\end{matrix}\right\rangle N - NO + H_2O.$$

These give the nitrosamine reaction with phenol and sulphuric acid; but are less stable than the nitrosamines of the secondary anilines. Reducing agents break off their nitroso-group.

Formanilide, $C_6H_5.NH.CHO$, is obtained on digesting aniline with formic acid, or by rapidly heating it together with oxalic acid:—

$$C_6H_5.NH_2 + C_2O_4H_2 = C_6H_6.NH.CHO + CO_2 + H_2O.$$

It consists of prisms, readily soluble in water, alcohol and ether. It melts at 46°, and continues liquid for some time. Concentrated sodium hydroxide precipitates the crystalline compound, $\left.\begin{matrix}C_6H_5\\CHO\end{matrix}\right\rangle NNa$, which is resolved by water into formanilide and NaOH. Silver nitrate added to the alcoholic solution of the sodium compound, precipitates *silver formanilide*, $C_6H_5.N{:}CH(OAg)$. When formanilide is distilled with concentrated hydrochloric acid, benzonitrile is produced (small quantity) (*Berichte*, 18, 1001):—

$$C_6H_5.NH.CHO = C_6H_5.CN + H_2O.$$

Dry HCl converts formanilide at 100° into diphenyl-methenylamidine (p. 621). The *alkyl formanilides*, $C_6H_5.NR(CHO)$, are produced when the alkyl iodides act upon sodium formanilide, or upon formanilide with NaOH (1 molecule) in alcoholic solution. They are odorless liquids which sustain a partial decomposition when distilled. They are resolved into acids and alkyl anilines when digested with alcoholic potash or with hydrochloric acid (*Berichte*, 21, 1107). The *alkyl isoformanilides*, $C_6H_5.N:CH.OAg$, compounds isomeric with the preceding, result when the alkyl iodides act upon silver formanilide (*Berichte*, 23, 2274, Ref. 659). P_2S_5 changes formanilide to *Thioformanilide*, $C_6H_5.NH.CHS$, which consists of white needles, melting at 137°, and decomposing at the same time into H_2S and phenylisocyanide, $C_6H_5.NC$. It is also formed when hydrogen sulphide acts upon phenylisocyanide (p. 260), or diphenyl-methylamidine; aniline is produced at the same time: $C_6H_5.N = CH — HN. C_6H_5 + H_2S = C_6H_5.NH.CHS + C_6H_5.NH_2$. Consult *Berichte*, 18, 2292, upon homologous thioformanilides.

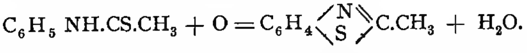
Acetanilide, $C_6H_5.NH.CO.CH_3$, is produced by boiling (equal molecules) aniline and glacial acetic acid together for several hours (*Berichte*, 15, 1977); the solid, crystalline mass is then distilled. It melts at 114° and boils at 295°, without decomposition. It is soluble in hot water, alcohol and ether. Sodium converts it into sodium acetanilide, $C_6H_5.N(Na).C_2H_3O$. Its hydrochloride is decomposed by water into acetanilide and hydrochloric acid. When the salt is heated to 250°, it yields diphenyl ethenylamidine (p. 621), at 280°, flavaniline, $C_{16}H_{14}N_2$ and at 300°, dimethyl quinoline (*Berichte*, 18, 1340). *o*-Amido-acetophenone, $C_6H_4(NH_2)CO.CH_3$, is produced when aniline is boiled with acetic anhydride and $ZnCl_2$. Ethylaniline, together with acetic acid, is the product on heating acetanilide with sodium alcoholate (*Berichte*, 19, 1356):—

$$C_6H_5.NH.CO.CH_3 + C_2H_5.ONa = C_6H_5.NH.C_2H_5 + (CH_3).CO_2Na.$$

p- and *o*-Di-substitution products (p. 596) are produced when chlorine, bromine and nitric acid act upon acetanilide; they yield mono-substituted anilines by saponification. *Monochloracetanilide* (1, 4) melts at 162°, the *dichlor* (1, 2, 4) at 140°, and both are formed by the action of bleaching lime (acidified with acetic acid) upon acetanilide. *Monobrom-acetanilide* (1, 4) melts at 165°; the *dibrom* (1, 2, 4) at 78°. *p-Nitroacetanilide* melts at 207° (Preparation, *Berichte*, 17, 222).

The isomeric *bromacetanilide*, $C_6H_5.NH.CO.CH_2.Br$ (melting at 131°), yields *indigo blue* when it is fused with caustic potash. It is very probable that pseudo-indoxyl, $C_6H_4\left\langle\begin{matrix}NH\\CO\end{matrix}\right\rangle CH_2$, is first produced (*Berichte*, 23, 57).

Thioacetanilide, $C_6H_5.NH.CS.CH_3$ or $C_6H_5.N:C\left\langle\begin{matrix}SH\\CH_3\end{matrix}\right.$ (p. 260), is obtained by heating acetanilide with phosphorus pentasulphide (*Berichte*, 19, 1071). It crystallizes from water in needles, melting at 75°. It is soluble in alkalies, but is separated again by acids. An alkaline solution of potassium ferricyanide oxidizes it to ethenyl amido-thiophenol (*Berichte*, 19, 1072):—



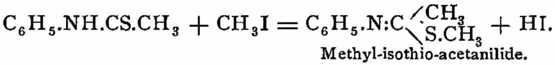
$$C_6H_5\ NH.CS.CH_3 + O = C_6H_4\left\langle\begin{matrix}N\\S\end{matrix}\right\rangle C.CH_3 + H_2O.$$

The analogous compounds react similarly. *Alkylized* thioacetanilides, *e.g.*, $C_6H_5.N(CH_3).CS.CH_3$, are obtained from the acetyl compounds of the secondary anilines (like acetmethyl-anilide ($C_6H_5.N(CH_3).CO.CH_3$), by heating them with P_2S_5 (*Berichte*, 15, 528):—

$$C_6H_5.N(CH_3).CO.CH_3 \quad \text{yields} \quad C_6H_5.N(CH_3).CS.CH_3.$$

Methyl-thioacetanilide, melts at 58–59°, and boils at 290°.

The derivatives of hypothetical *isothioacetanilide*, $C_6H_5.N{:}C\Big<\begin{matrix}CH_3\\SH\end{matrix}$ (p. 260), are isomeric with the above. They are obtained by the action of sodium alcoholate and alkyl iodides upon thioacetanilide (similar to formation of phenyl-isothio-urethanes, p. 615, and of phenyl-isothio-ureas, p. 617):—



$$C_6H_5.NH.CS.CH_3 + CH_3I = C_6H_5.N{:}C\Big<\begin{matrix}CH_3\\S.CH_3\end{matrix} + HI.$$

Methyl-isothio-acetanilide.

The *methyl* compound boils at 245°, the *ethyl* at 250°. These decompose into aniline hydrochloride and thioacetic ester, $CH_3.CO.SR$, when shaken with hydrochloric acid.

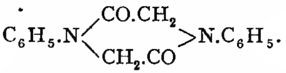
ANILIDO-ACIDS.—PHENYLAMIDO-ACIDS.

Anilido-formic Acid, $C_6H_5.NH.CO_2H$, is carbanilic acid (p. 612).

Anilido-acetic Acid, $C_6H_5.NH.CH_2.CO_2H$, **Phenyl glycocoll, Phenylglycin**, is obtained from chlor- or brom-acetic acid by the action of aniline (2 molecules) and water (*Berichte*, 10, 2046; see, also, *Berichte*, 21, Ref. 136). It forms indistinct crystals, melting at 127°.

Its alkyl esters are produced when aniline is heated with the diazo-acetic esters (p. 374). If the free acid be heated to 140–150°, it passes into the *anhydride* $(C_6H_5.N.CH_2.CO)_2$, which is insoluble in water, and melts at 263°.

It is identical with diphenyl-diacipiperazine (*Berichte*, 22, 1786, 1795):—



$$C_6H_5.N\Big<\begin{matrix}CO.CH_2\\CH_2.CO\end{matrix}\Big>N.C_6H_5.$$

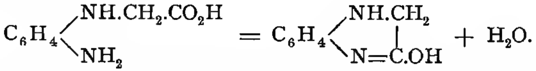
Indigo blue results upon fusing a mixture of phenylglycin and caustic potash with air access. It is very probable that pseudoindoxyl, $C_6H_4\Big<\begin{matrix}CO\\NH\end{matrix}\Big>CH_2$, is formed at first, but is then oxidized to indigo (*Berichte*, 23, 3044).

Nitrous acid converts phenylglycin into **Nitroso-phenylglycin**, $C_6H_5.N(NO).CH_2.CO_2H$. This may be reduced to an amido-compound, *identical* with the phenylhydrazone of glyoxylic acid, $C_6H_5.NH.N{:}CH.CO_2H$ (p. 330).

Phenylhydantoïn, $C_6H_5.N\Big<\begin{matrix}CH_2.CO\\CO.NH\end{matrix}\Big>$, results upon heating phenylglycin and urea to 100°. It forms delicate needles, melting at 191°. **α-Phenylhydantoïn**, $C_6H_5.CH\Big<\begin{matrix}CO.NH\\NH.CO\end{matrix}\Big>$, is isomeric with the preceding. It may be obtained from benzaldehyde-cyanhydrin and urea (p. 392). It melts at 178° (*Berichte*, 21, 2321).

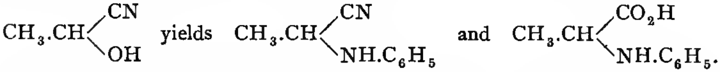
Indol, results upon distilling a mixture of the calcium salt of phenylglycocoll and calcium formate (*Berichte*, 22, Ref. 579). In the same manner, *o*-tolindol is obtained from *o*-tolylglycocoll (*Berichte*, 23, Ref. 654).

o-**Nitrophenyl Glycocoll**, $C_6H_4(NO_2).NH.CH_2.CO_2H$, formed by heating *o*-nitraniline with bromacetic acid to 130°, crystallizes in dark red prisms, melting at 193°. When it is reduced by tin and hydrochloric acid, it forms an amido-derivative. The latter condenses to oxy-dihydroquinoxaline, with separation of water (*Berichte*, 19, 7):—



$$C_6H_4\left\langle\begin{array}{l}NH.CH_2.CO_2H\\ NH_2\end{array}\right. = C_6H_4\left\langle\begin{array}{l}NH.CH_2\\ \quad\ \ |\\ N{=}C.OH\end{array}\right. + H_2O.$$

The higher anilido-fatty acids are similarly prepared from aniline and the brom-fatty acids. They can (their nitriles) also be formed from the cyanhydrins of the aldehydes by digesting them with aniline. Thus, ethidene cyanhydrin yields a nitrite, that upon saponification with hydrochloric acid becomes α-anilido-propionic acid (*Berichte*, 15, 2034):—



$$CH_3.CH\left\langle\begin{array}{l}CN\\ OH\end{array}\right. \text{ yields } CH_3.CH\left\langle\begin{array}{l}CN\\ NH.C_6H_5\end{array}\right. \text{ and } CH_3.CH\left\langle\begin{array}{l}CO_2H\\ NH.C_6H_5.\end{array}\right.$$

The *esters* of the anilido-fatty acids are produced by heating diazo-fatty acid esters with aniline (p. 374):—

$$C_6H_5.NH_2 + CH(N_2).CO_2R = C_6H_5.NH.CH_2.CO_2R + N_2.$$

α-**Anilido-propionic Acid**, Phenylalanine, consists of colorless laminæ, melting at 162°. They turn red on exposure to the air.

Anil-pyroracemic Acid, $C_6H_5.N{:}C(CH_3).CO_2H$, is formed from pyro-racemic acid and aniline (2 molecules). Boiling water converts it into anil-uvitonic acid, $C_{11}H_9NO_2$, a derivative of quinoline, which yields methyl-quinoline, $C_9H_6(CH_3)N$, when distilled with lime (*Berichte*, 16, 2359).

By heating aniline and aceto-acetic ester to 120–135° **Acetoacetanilide**, $CH_2\left\langle\begin{array}{l}CO.CH_3\\ CO.NH.C_6H_5\end{array}\right.$, is produced. It melts at 85° (*Annalen*, 236, 75). When warmed with sulphuric acid it splits off water and condenses to γ-methyl carbostyril (*Berichte*, 21, 625).

When aniline and aceto-acetic ester interact at the ordinary temperature there is formed anil-aceto-acetic ester, that may be considered as β-**Phenylimido-crotonic Ester**, $CH_3.C(NH.C_6H_5){:}CH.CO_2.R$ (p. 339), or β-**Phenylamido-crotonic Ester**, $C_6H_5.NH.C\left\langle\begin{array}{l}CH_3\\ CH.CO_2R\end{array}\right.$ (*Berichte*, 20, 1397; 21, 1965). This is a thick oil. Acids and alkalies decompose it into its components. If it is heated to 200° it loses alcohol and condenses to γ-oxyquinaldine, $C_{10}H_9NO$, and phenyl lutidon-carboxylic acid, $C_{14}H_{13}NO_3$ (*Berichte*, 20, 947 and 1398). The latter is also formed on heating with methyl iodide (*Berichte*, 22, 83).

Toluidines, etc., react in a similar manner with aceto-acetic esters. The products are tolylamidocrotonic esters, etc., which by condensation form γ-oxyquinaldine derivatives (*Berichte*, 21, 523).

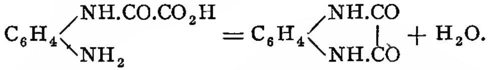
β-**Anilido-pyrotartaric Acid**, $\begin{array}{l}C_6H_5.NH.C(CH_3).CO_2H,\\ \qquad\quad\ |\\ \qquad\ CH_2.CO_2H\end{array}$ is formed when prussic acid and aniline act upon aceto-acetic ester (*Berichte*, 23, 893). It melts at 102°, and when heated to 180° yields citraconanile (p. 611, see *Berichte*, 23, 542).

ANILIDES OF DIBASIC ACIDS.

Oxanilide, $C_2O_2\left\langle\begin{matrix}NH.C_6H_5\\NH.C_6H_5\end{matrix}\right.$, diphenyl-oxamide, is obtained by heating aniline (2 molecules) with oxalic acid (1 molecule) to 180°. It consists of pearly leaflets, melting at 245° and boiling near 360°. It dissolves readily in benzene, but with difficulty in hot alcohol.

Oxanilic Acid, $C_2O_2\left\langle\begin{matrix}NH.C_6H_5\\OH\end{matrix}\right.$, is formed by heating aniline with excess of oxalic acid to 140° (*Berichte*, 23, 1820). It crystallizes in leaflets, dissolves in water, reacts acid, and conducts itself like a monobasic acid.

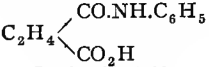
p-**Nitro-oxanilic Acid,** $C_6H_4(NO_2).NH.CO.CO_2H$ (with some ortho-product), is obtained by nitrating oxanilic acid. It melts at 210°. *o*-**Nitro-oxanilic Acid** is more easily obtained by fusing a mixture of *o*-nitraniline and oxalic acid at 140°. It crystallizes in yellow needles and melts at 120° (*Berichte*, 19, 2936). Tin and hydrochloric acid reduce it to *o*-**Amido-oxanilic Acid,** which loses water and immediately condenses to dioxyquinoxaline:—



$$C_6H_4\left\langle\begin{matrix}NH.CO.CO_2H\\NH_2\end{matrix}\right. = C_6H_4\left\langle\begin{matrix}NH.CO\\ |\\NH.CO\end{matrix}\right. + H_2O.$$

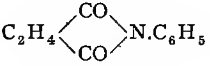
In a similar manner nitro-oxalyl toluidic acid (from nitrotoluidine and oxalic acid), $C_6H_3(CH_3)\left\langle\begin{matrix}NH.CO.CO_2H\\NO_2\end{matrix}\right.$, yields dioxymethylquinoxaline (*Berichte*, 17, 318; 19, 671).

The anilides of the higher di- and poly-basic acids may be easily prepared by heating their anhydrides with aniline. PCl_5 converts them into acid *aniles* (*Berichte*, 21, 957):—



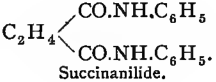
$$C_2H_4\left\langle\begin{matrix}CO.NH.C_6H_5\\CO_2H\end{matrix}\right.$$

Succinanilic Acid.



$$C_2H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle N.C_6H_5$$

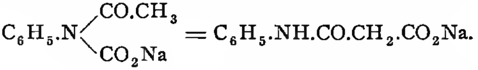
Succinanile.



$$C_2H_4\left\langle\begin{matrix}CO.NH.C_6H_5\\CO.NH.C_6H_5.\end{matrix}\right.$$

Succinanilide.

Malonanilic Acid, $CH_2\left\langle\begin{matrix}CO.NH.C_6H_5\\CO_2H\end{matrix}\right.$, is produced by a peculiar transposition of acetylphenyl carbaminate of sodium when heated to 140° (*Berichte* 18, 1359):—



$$C_6H_5.N\left\langle\begin{matrix}CO.CH_3\\CO_2Na\end{matrix}\right. = C_6H_5.NH.CO.CH_2.CO_2Na.$$

The acid crystallizes in needles, melting at 132° and decomposing into CO_2 and acetanilide. PCl_5 converts it into trichlorquinoline (*Berichte*, 17, 740; 18, 2975). Malonic acid and toluidine yield malon-toluidic acid, from which trichlormethylquinoline may be obtained (*Berichte*, 18, 2979).

Succinanilic Acid melts at 148°. When heated higher it decomposes into water and **Succinanile,** $C_2H_4(CO)_2.N.C_6H_5$, melting at 150°, and boiling at 400°.

Maleïnanilide, $C_2H_2(CO.NH.C_6H_5)_2$, results upon digesting maleïc acid with aniline. It melts at 211°. **Fumaranilide,** $C_2H_2(CO.NH.C_6H_5)_2$, is produced when aniline is heated together with malic acid. It melts at 87°.

Citraconanile, $C_5H_4O_2{:}N.C_6H_5$, from citraconic and mesaconic acids with aniline, is also formed in the distillation of anilido-pyrotartaric acid (p. 609). It melts at 96° (*Berichte*, 23, 891).

Phthalanile, $C_6H_4(CO)_2N.C_6H_6$, from aniline and phthalic acid, melts at 205°. It is used in effecting different syntheses.

ANILIDES OF CARBONIC ACID.

Diphenyl urea, $CO\Big\langle\begin{array}{l}NH.C_6H_5\\NH.C_6H_5\end{array}$, carbanilide, is formed by the action of phosgene gas on aniline (*Berichte*, 16, 2301):—

$$COCl_2 + 2C_6H_5.NH_2 = CO(NH.C_6H_5)_2 + 2HCl;$$

by the union of carbanile (p. 612) with aniline:—

$$CO{:}N.C_6H_5 + NH_2.C_6H_6 = CO(NH.C_6H_5)_2;$$

by the action of mercuric oxide or alcoholic KOH upon diphenyl thio-urea (p. 616):—

$$CS(NH.C_6H_5)_2 + HgO = CO(NH.C_6H_5)_2 + HgS;$$

and by heating aniline (3 parts) with urea (1 part) to 150–180°:—

$$CO(NH_2)_2 + 2NH_2.C_6H_5 = CO(NH.C_6H_5)_2 + 2NH_3.$$

It is most readily obtained by heating carbanilamide with aniline to 190° (*Berichte*, 9, 820), or by heating diphenyl carbonate with aniline to 150–180° (*Berichte* 18, 516):—

$$CO(O.C_6H_5)_2 + 2NH_2.C_6H_5 = CO(NH.C_6H_5)_2 + 2C_6H_5.OH.$$

Carbanilide consists of silky needles, easily soluble in alcohol and ether, but sparingly soluble in water. It melts at 235° and distils at 260°. When boiled with alkalies it decomposes into aniline and urea. Triphenyl-guanidine is produced on heating it with sodium ethylate to 220° (*Berichte*, 16, 2301).

Diphenyl Urea Chlorides (p. 376) (*Berichte*, 23, 424), are produced when $COCl_2$ acts upon secondary anilines, such as diphenylamine:—

$$COCl_2 + NH(C_6H_5)_2 = CO\Big\langle\begin{array}{l}N(C_6H_5)_2\\Cl\end{array} + HCl.$$

Diphenyl urea Chloride, $(C_6H_5)_2\,N.COCl$, crystallizes in white laminæ, melting at 85°. When these urea chlorides act upon benzene in the presence of $AlCl_3$ they form the *diphenylamides* of aromatic acids—

$$(C_6H_5)_2N.COCl + C_6H_6 = (C_6H_5)_2N.CO.C_6H_5 + HCl,$$

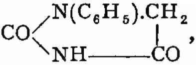
which pass into acids and diphenylamine on warming with hydrochloric acid (*synthesis of aromatic acids*, *Berichte*, 20, 2118). Thiophosgene acts like $COCl_2$. It converts the secondary anilines into *Thiourea chlorides*, *e.g.*, $(C_6H_5)_2N.CSCl$, and *Thiocarbanilides*, *e. g.*, $CS\Big\langle\begin{array}{l}N(C_6H_5)_2\\N(C_6H_5)_2\end{array}$ (*Berichte*, 21, 102). Diphenyl urea chloride heated to 100°, with alcoholic ammonia, yields unsymmetrical **diphenyl** urea, $CO\Big\langle\begin{matrix}N(C_6H_5)_2\\NH_2\end{matrix}$. Long needles, melting at 189°, and when distilled yielding diphenylamine and cyanic acid. If the chloride be heated with aniline we get **Triphenyl urea**, $CO\Big\langle\begin{matrix}N(C_6H_5)_2\\NHC_6H_5\end{matrix}$. It is also produced by mixing phenylisocyanate with diphenylamine. It crystallizes in needles, melting at 136°. Mixed phenyl ureas are obtained in the same manner (*Berichte*, 17, 2092). The action of diphenylamine upon diphenyl urea chloride produces **tetraphenyl urea**, $CO\Big\langle\begin{matrix}N(C_6H_5)_2\\N(C_6H_5)_2\end{matrix}$. Crystals melting at 183°.

Phenylurea, $CO\Big\langle\begin{matrix}NH.C_6H_5\\NH_2\end{matrix}$, **Carbanilamide**, is obtained like the alkylic ureas (p. 388): by conducting vapors of cyanic acid into aniline; $CO:NH + C_6H_5.NH_2 = CO\Big\langle\begin{matrix}NH.C_6H_5\\NH_2\end{matrix}$; and by the action of ammonia upon carbanile:—

$$CO:N.C_6H_5 + NH_3 = CO\Big\langle\begin{matrix}NH.C_6H_5\\NH_2\end{matrix}.$$

It is best prepared by evaporating the aqueous solution of aniline hydrochloride and potassium isocyanide (*Berichte*, 9, 820). It forms needles easily soluble in hot water, alcohol and ether and melting at 144–145°. If boiled with caustic potash it breaks up into aniline, ammonia and cyanuric acid.

Esters of isocyanic acid convert aniline into alkylized phenyl ureas, *e. g.*, $CO\Big\langle\begin{matrix}NH.C_6H_5\\NH.C_2H_5\end{matrix}$, ethyl phenylurea.

Glycolyl-phenylurea,  $CO\Big\langle\begin{matrix}N(C_6H_5).CH_2\\ |\\NH\text{———}CO\end{matrix}$, phenyl-hydantoïn (p. 392), is obtained on heating phenylglycocoll (p. 608) to 160° with urea. It consists of needles, melting at 191°.

Carbanilic Acid, $CO\Big\langle\begin{matrix}NH.C_6H_5\\OH\end{matrix}$, **phenyl carbamic acid**, is not known in a free state. Its esters, called **phenyl urethanes**, (p. 383) result in the action of chlorcarbonic esters upon aniline (most easily by shaking the two compounds with water (*Berichte*, 18, 978), or of carbanile upon alcohols and phenols:—

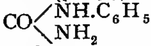
$$CO:NC_6H_5 + C_2H_5.OH = CO\Big\langle\begin{matrix}NH.C_6H_5\\O.C_2H_5\end{matrix}.$$

The *ethyl ester* melts at 52° and boils at 237°, decomposing partially into $CO:N.C_6H_5$ and $C_2H_5.OH$, which reunite on standing. Diphenylurea is formed on heating with potash or with aniline. The *methyl ester* melts at 47°, and is converted into amidosulphobenzoic ester when dissolved in sulphuric acid (*Berichte*, 18, 980):—

$$C_6H_5.NH.CO_2.CH_3 + SO_4H_2 = C_6H_3\begin{cases}NH_2\\SO_3H\\CO_2CH_3\end{cases} + H_2O.$$

The *phenyl ester*, $C_6H_5.NH.CO_2.C_6H_5$, is formed when carbanile is heated with phenol (readily in the presence of $AlCl_3$). It melts at 124° (*Berichte*, 18, 875).

Carbanile, $CO:N.C_6H_5$, **phenyl isocyanate**, is produced in the distillation of oxanilide, or better oxanilic esters with P_2O_5, also from diazobenzene salts, $C_6H_5.N_2X$, by the action of potassium cyanate and copper (*Berichte*, 23, 1225). It may be most readily obtained by leading $COCl_2$ into fused aniline hydrochloride

(*Berichte*, 17, 1284), or by heating phenyl mustard oil to 170° with HgO (*Berichte*, 23, 1536). It is a mobile liquid, boiling at 163° and has a pungent odor, provoking tears. Carbanile is perfectly analogous to the isocyanic esters in chemical deportment (p. 274). It yields diphenylurea with water. With ammonia carbanilamide,  $CO\begin{matrix}\diagup NH.C_6H_5\\ \diagdown NH_2\end{matrix}$, is formed; with the amines we obtain corresponding alkyl compounds.

It unites with polyhydric alcohols and phenols to form carbanilic esters. This is a reaction that can be employed in determining alcoholic hydroxyls (*Berichte*, 18, 2428 and 2606).

Phenylisocyanate acts in a similar manner upon aldoximes and ketoximes (p. 205). The hydrogen of its hydroxyl group is replaced (*Berichte*, 22, 3101, 3109; 23, 2163):—

$$C_6H_5.CH{:}N.OH + CON.C_6H_5 = C_6H_5.CH{:}N.O.CO.NH.C_6H_5.$$

However, carbonyl compounds (with the group CO) do not react with phenylisocyanate. The reaction, therefore, can be employed for the purpose of determining constitution (*Berichte*, 23, 257).

Phenylisocyanate also reacts with the sulphydrate group SH; the CS-group is without action (*Berichte*, 23, 272).

Diazo-amido-compounds, *e.g.*, $C_6H_6.N_2.NHR$, react with phenylisocyanate. In so doing, the hydrogen of the amido-group is replaced (*Berichte*, 22, 3109).

The preceding reactions, occurring in the absence of water (thus avoiding electrolytic dissociation), proceed in the normal way. Rearrangements do not take place, hence they are well adapted for the determination of constitution (Goldschmidt, *Berichte*, 23, 2179).

On heating phenylisocyanate with benzene and $AlCl_3$, we get benzoylanilides:—

$$C_6H_5.N{:}CO + C_6H_6 = C_6H_5.NH.CO.C_6H_5.$$

Phenylisocyanate can be polymerized by heating it with potassium acetate (*Berichte*, 18, 764), when there is formed

Triphenylisocyanurate, $(CON)_3(C_6H_5)_3$ (p. 276). It is also obtained upon heating triphenylisomelamine (p. 620) with concentrated hydrochloric acid to 150° C. (*Berichte*, 18, 3225):—

$$C_3N_3(C_6H_5)_3(NH)_3 + 3H_2O = C_3O_3N_3(C_6H_5)_3 + 3NH_3.$$

It crystallizes from alcohol in white needles, melting at 275°. Its isomeride is

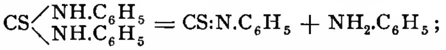
Triphenylcyanurate, $C_3N_3(O.C_6H_5)_3$. The action of cyanogen chloride or cyanuric chloride upon sodium phenate, produces this:—

$$3C_6H_5.O.Na + C_3N_3Cl_3 = C_3N_3(O.C_6H_5)_3 + 3NaCl.$$

It crystallizes in long needles, melting at 224°.

Phenyl Isocyanide, $C_6H_5.NC$, phenyl carbylamine, is isomeric with benzonitrile, $C_6H_5.CN$ (p. 287), and is produced by the action of chloroform on aniline in an alcoholic solution of KOH (*Berichte*, 10, 1096), or by the distillation of diphenyl-methenyl-amidine (p. 621), and of thioformanilide, $C_8H_5.NH.CSH$. It is a liquid, resembling prussic acid, with pungent odor and boiling at 167° with partial decomposition. It is dichroic, being blue in reflected and green in transmitted light. Alkalies do not affect it, but acids convert it into aniline and formic acid. Heated to 220°, it passes into isomeric benzonitrile, $C_6H_5.CN$. It combines with H_2S, forming thioformanilide (p. 607).

Phenyl Mustard Oil, Sulpho-carbanile, $CS:N.C_6H_5$ (p. 280), is obtained by boiling diphenyl thio-urea (p. 616) with sulphuric or concentrated hydrochloric acid, or, what would be best, with a concentrated phosphoric acid solution (*Berichte*, 15, 986):— .



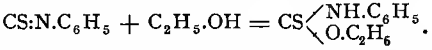
$$\mathrm{CS}\Big\langle\begin{matrix}\mathrm{NH.C_6H_5}\\ \mathrm{NH.C_6H_5}\end{matrix} = \mathrm{CS{:}N.C_6H_5} + \mathrm{NH_2.C_6H_5};$$

and by the action of an alcoholic iodine solution (with triphenyl guanidine, *Berichte*, 9, 812), or $CSCl_2$, upon aniline. It is a colorless liquid, with an odor resembling that of mustard oil, and boils at 222°. It is converted into benzonitrile when heated with reduced copper or zinc-dust:—

$$\mathrm{C_6H_5.N{:}CS} + \mathrm{Cu} = \mathrm{C_6H_5.CN} + \mathrm{CuS}.$$

On this reaction is founded a procedure to replace the group NH_2 by COOH, that is, to convert the anilines successively into thio-ureas, mustard oils, nitriles and acids. Benzonitrile (with aniline) is also produced by directly heating diphenyl thio-urea with zinc dust (*Berichte*, 15, 2505).

In all its reactions, it is analogous to the mustard oils of the fatty series. If heated with anhydrous alcohols to 120°, or by the action of alcoholic potash, it is converted into phenyl-thio-urethanes (p. 386):—



$$\mathrm{CS{:}N.C_6H_5} + \mathrm{C_2H_5.OH} = \mathrm{CS}\Big\langle\begin{matrix}\mathrm{NH.C_6H_5}\\ \mathrm{O.C_2H_5}\end{matrix}.$$

It forms phenyl-thio-ureas with ammonia, the amines and the anilines.

Phenyl-sulphocyanate, $C_6H_5.S.CN$, is isomeric with phenyl mustard oil. It is formed when hydrosulphocyanic acid acts upon diazobenzene sulphate (see this), and cyanogen chloride upon the lead salt of methyl mercaptan:—

$$\mathrm{(C_6H_5.S)_2Pb} + 2\mathrm{CNCl} = 2\mathrm{C_6H_5.S.CN} + \mathrm{PbCl_2}.$$

It is a colorless liquid, boiling at 231°, and in its reactions is analogous to the sulphocyanic esters (p. 280).

Methenyl-amido Thiophenol, $C_6H_4\Big\langle\begin{matrix}S\\N\end{matrix}\Big\rangle CH$, derived from ortho-amido thiophenol, $C_6H_4\Big\langle\begin{matrix}SH\\NH_2\end{matrix}$, is a base, and is isomeric with phenyl sulphocyanate and phenyl mustard oils. See Amido-phenols.

Derivatives of *Dithiocarbamic Acid* (p. 386).

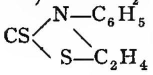
Phenyl Dithiocarbamic Acid, $CS\Big\langle\begin{matrix}NH.C_6H_5\\SH\end{matrix}$. Its potassium salt is formed when potassium xanthate (p. 381) is boiled with aniline and alcohol. It consists of golden yellow needles. When the acid is liberated from its salts it decomposes into aniline and CS_2. Its *esters*—the normal dithio-urethanes (p. 386 and *Berichte*, 15, 563)—are produced by warming phenyl mustard oil with mercaptans:—

$$\mathrm{C_6H_5.N{:}CS} + \mathrm{CH_3.SH} = \mathrm{C_6H_5.NH.CS.S.CH_3};$$

and from the alkyl compounds of diphenyl isothio-urea when heated with CS_2 (p. 617). The *methyl ester* melts at 87–88°; the *ethyl* (**Phenyl dithio-urethane**) at 60°.

When these dithio-urethanes are heated they decompose into phenyl mustard oil and mercaptans. They dissolve in alkalies, and on warming part with mercaptans (*Berichte*, 15, 1305). Completely alkylized dithio-urethanes, having the imide hydrogen replaced by alkyls, are formed the same as the mono-alkyl derivatives, *i. e.*, by heating alkylized diphenyl-amidine-thioalkyls (p. 617) to 150° with CS_2. **Ethyl Phenyldithiourethane,** $CS\left\langle\begin{matrix}N(C_2H_5).C_6H_5\\S.C_2H_5\end{matrix}\right.$, melts at 68.5°, and boils at 310°. These compounds are very stable, no longer soluble in alkalies, and are not desulphurized by mercuric oxide or an alkaline lead solution. They form so-called addition products (*Berichte*, 15, 568 and 1308) with methyl iodide. Phenyl sulphurethane and diphenyl-thio-urea (p. 618) do the same.

An analogous compound is formed on heating diphenylamidin-thio-ethylene (p. 618) with CS_2. The product is called **Ethylene-Phenyl-dithiocarbamate,**



$CS\left\langle\begin{matrix}N—C_6H_5\\S—C_2H_4\end{matrix}\right.$ (*Berichte*, 15, 345).

Derivatives of *Sulphocarbamic Acid*, $CS\left\langle\begin{matrix}NH_2\\OH\end{matrix}\right.$, *thio-carbaminic acid*, $CO\left\langle\begin{matrix}NH_2\\SH\end{matrix}\right.$, and the hypothetical *imidothiocarbonic acid*, $NH:C\left\langle\begin{matrix}OH\\SH\end{matrix}\right.$ (p. 384).

Ethyl Phenylsulphocarbamate, Phenyl-thiourethane, $CS\left\langle\begin{matrix}NH.C_6H_5\\O.C_2H_5\end{matrix}\right.$ (Phenyl xanthamide) (*Berichte*, 15, 1307), is formed by heating phenyl-mustard-oil with alcohol (*Berichte*, 15, 2164):—

$$C_6H_5.N:CS + C_2H_5.OH = C_6H_5.NH.CS.O.C_2H_5.$$

It melts at 71–72°, and is resolved into phenyl-mustard-oil and alcohol when distilled. It is soluble in alkalies, and unites with mercury, silver and lead.

When alkyl iodides act upon these metallic compounds (not the free phenyl-sulphurethanes) we obtain *phenyl-isothiourethanes*, the alkyl derivatives of *phenyl imido thio-carbonic acid* (see above). The reaction is very probably analogous to that occurring with thioacetanilides (p. 607) and the phenyl sulpho-ureas (p. 617):—

$$C_6H_5.NK.CS.O.C_2H_5 + CH_3I = C_6H_5.N:C\left\langle\begin{matrix}O.C_2H_5\\S.CH_3\end{matrix}\right. + KI.$$

The *methyl* derivative is a liquid, and boils with partial decomposition at 260°. The *ethyl* compound melts at 30° and boils at 278–280°.

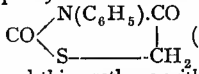
These alkyl derivatives are soluble in concentrated hydrochloric acid, and are precipitated by water. When heated with hydrochloric acid, they revert again to phenyl sulphurethane and alkyl chlorides; heated with dilute sulphuric acid to 200°, aniline and thiocarbonic esters, *e.g.*, $CO\left\langle\begin{matrix}O.C_2H_5\\S.CH_3\end{matrix}\right.$, result.

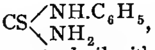
On oxidizing phenylsulphurethane, in alkaline solution, with ferricyanide of potassium, so-called *ethoxyyphenyl mustard oil*—a derivative of *o*-amido-thiophenol (see this) (*Berichte*, 19, 1811), is formed:—

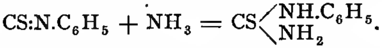
$$C_6H_5.N:C\left\langle\begin{matrix}O.C_2H_5\\SH\end{matrix}\right. + O = C_6H_4\left\langle\begin{matrix}N\\S\end{matrix}\right\rangle CO.C_2H_5 + H_2O.$$

The esters of *phenylthiocarbaminic acid* (see above) *e.g.*, $CO\left\langle\begin{matrix}NH.C_6H_5\\S.CH_3\end{matrix}\right.$, are obtained by heating the thio- alkyl-diphenylamidines (p. 617) with dilute sulphuric acid to 180° (*Berichte*, 15, 339).

The *methyl ester* melts at 83–84°; the *ethyl ester* at 73°. Warm alkalies resolve them into aniline, carbon dioxide and mercaptans.

Another derivative of phenyl thio-carbaminic acid is the so-called **glycolide of Phenyl-mustard-oil**,  $CO\left<\begin{matrix}N(C_6H_5).CO\\ \quad\quad | \\ S\text{———}CH_2\end{matrix}\right.$ (p. 398), which is formed by heating phenyl-mustard-oil or phenyl-thio-urethane with chloracetic acid and alcohol to 160°; also by boiling diphenylthiohydantoïn and (ortho) phenylthiohydantoïn (p. 618) with hydrochloric acid (*Berichte*, 14, 1663). It crystallizes from water in laminæ, melting at 148° and decomposing, on boiling with baryta, into aniline, carbon dioxide and thioglycollic acid.

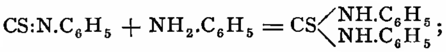
Phenylthiurea,  $CS\left<\begin{matrix}NH.C_6H_5\\NH_2\end{matrix}\right.$, Sulphocarbanilamide (p. 395), is formed by the union of phenyl-mustard-oil with ammonia:—



$$CS{:}N.C_6H_5 + NH_3 = CS\left<\begin{matrix}NH.C_6H_5\\NH_2\end{matrix}\right..$$

It crystallizes in needles, melting at 154°, and forms a double salt with $PtCl_4$. S is replaced by O and phenylurea formed on boiling with silver nitrate.

Diphenyl-thiurea,  $CS\left<\begin{matrix}NH.C_6H_5\\NH.C_6H_5\end{matrix}\right.$, sulphocarbanilide, is produced by the union of phenyl-mustard-oil with aniline in an alcoholic solution:—



$$CS{:}N.C_6H_5 + NH_2.C_6H_5 = CS\left<\begin{matrix}NH.C_6H_5\\NH.C_6H_5\end{matrix}\right.;$$

it is also obtained by boiling aniline (1 molecule) with CS_2 and alcoholic potash (1 molecule):—

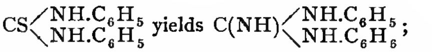
$$CS_2 + 2NH_2.C_6H_5 = CS(NH.C_6H_5)_2 + SH_2;$$

the product is poured into dilute hydrochloric acid, the alcohol evaporated and the mass crystallized from alcohol.

Diphenylthiurea consists of colorless, shining leaflets, melting at 151° (*Berichte*, 19, 1821), and readily soluble in alcohol. An alcoholic iodine solution converts it into sulpho-carbanile and triphenyl-guanidine. When boiled with concentrated hydrochloric acid or phosphoric acid, it decomposes into phenyl-mustard-oil and aniline (p. 614); the mixed thiureas, containing two dissimilar benzene residues and resulting from the phenyl-mustard-oils and anilines (see above), undergo, under like treatment, a decomposition into two mustard-oils and two anilines (*Berichte*, 16, 2016).

S is replaced by O, and the product is diphenylurea, if diphenyl thiurea be boiled with alcoholic soda or mercuric oxide (p. 611); monophenyl thiurea, on the contrary, has hydrogen sulphide removed and becomes phenylcyanamide (p. 395). In a benzene solution mercuric oxide produces carbodiphenylimide (p. 620).

In the action of alcoholic ammonia and lead oxide NH replaces S, forming diphenyl-guanidine (p. 395):—



$$CS\left<\begin{matrix}NH.C_6H_5\\NH.C_6H_5\end{matrix}\right. \text{ yields } C(NH)\left<\begin{matrix}NH.C_6H_5\\NH.C_6H_6\end{matrix}\right.;$$

under like circumstances triphenyl-guanidines are formed with anilines.

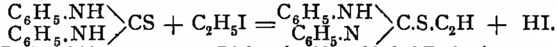
Phenyl- and diphenyl-thiurea are soluble in alkalies, because metallic compounds are probably formed by the replacement of hydrogen of the imide-group (as in the case of thioacetanilide, $C_6H_5.NH.CS.CH_3$ p. 607). If this be true they have not yet been isolated. Acids again set free the phenylureas.

See *Berichte*, 17, 2088 and 3033 upon the alkyl phenyl thiureas and triphenyl thiureas. When the phenylthiureas are heated with amines secondary amine residues are displaced by primary amine residues (*Berichte*, 17, 3044).

Tetraphenylthiurea, $CS\begin{matrix}\diagup N(C_6H_5)_2\\ \diagdown N(C_6H_5)_2\end{matrix}$, is obtained by heating symmetrical tetra-phenylguanidine (p. 619) with carbon disulphide. It crystallizes in long, shining needles, which melt at 195° (*Berichte*, 15, 1530).

Derivatives of hypothetical *Isothiourea*, $\begin{matrix}NH_2\\ NH\end{matrix}\!\!>\!C.SH$ (Imidothiocarbamic acid, amidine thiohydryl, p. 394, *Berichte*, 21, 1860).

The *diphenyl thioalkyl* derivatives (their haloid salts) are obtained by the action of caustic alkali and alkyl iodides upon diphenylthiurea, or better by heating the latter with an alcoholic solution of the alkyl iodides (bromides) (*Berichte*, 14, 1489 and 1755; 21, 963; *Annalen*, 211, 85):—

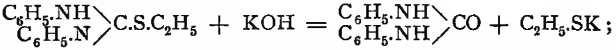


$$\begin{matrix}C_6H_5.NH\\ C_6H_5.NH\end{matrix}\!\!>\!CS + C_2H_5I = \begin{matrix}C_6H_5.NH\\ C_6H_5.N\end{matrix}\!\!>\!C.S.C_2H + HI.$$

Diphenylthiurea. Diphenylamidine-thiethyl Derivative.

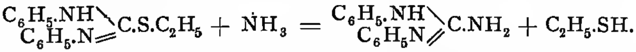
Alkalies set free the bases, which are soluble in alcohol and combine with 1 equivalent of acid to form crystalline salts.

The *methyl* compound (*Diphenylamidine-Thiomethyl*) melts at 110°; the *ethyl* derivative at 73°. If heated with alcoholic potash it splits up into diphenylurea and potassium mercaptide:—



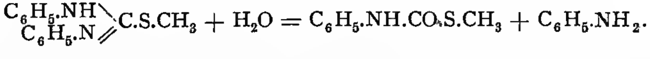
$$\begin{matrix}C_6H_5.NH\\ C_6H_5.N\end{matrix}\!\!>\!C.S.C_2H_5 + KOH = \begin{matrix}C_6H_5.NH\\ C_6H_5.NH\end{matrix}\!\!>\!CO + C_2H_5.SK;$$

and when heated to 120° with alcoholic ammonia diphenyl-guanidine (p. 619) and mercaptan are obtained:—



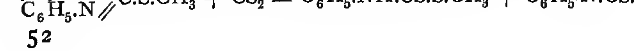
$$\begin{matrix}C_6H_5.NH\\ C_6H_5.N\end{matrix}\!\!>\!C.S.C_2H_5 + NH_3 = \begin{matrix}C_6H_5.NH\\ C_6H_5N\end{matrix}\!\!>\!C.NH_2 + C_2H_5.SH.$$

The alkyl derivatives yield carbo-diphenylimide $\begin{matrix}C_6H_5.N\\ C_6H_5.N\end{matrix}\!\!>\!C$ (p. 620), and mercaptan when distilled; and when heated to 180°, with dilute sulphuric acid, they decompose into phenylthio-carbamic esters (p. 615), and aniline:—



$$\begin{matrix}C_6H_5.NH\\ C_6H_5.N\end{matrix}\!\!>\!C.S.CH_3 + H_2O = C_6H_5.NH.CO.S.CH_3 + C_6H_5.NH_2.$$

If heated with carbon disulphide to 160° the products are phenyl-mustard oil, and phenyl-dithiocarbamic esters (*Berichte*, 15, 338):—

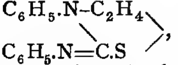


$$\begin{matrix}C_6H_5.NH\\ C_6H_5.N\end{matrix}\!\!>\!C.S.CH_3 + CS_2 = C_6H_5.NH.CS.S.CH_3 + C_6H_5.N{:}CS.$$

The last two decompositions are perfectly analogous to those of the amidines (p. 293).

When the diphenylamidine-thioalkyls are heated with alkyl iodides, their alkyl derivatives result, *e. g.*, $\left.\begin{array}{l}C_6H_5.N(CH_3)\\ C_6H_5.N\end{array}\right\rangle C.S.C_2H_5$. These yield dialkylic dithio-urethanes with carbon disulphide (p. 615).

Diphenylthiurea also reacts with benzyl chloride, $C_6H_5.CH_2Cl$. Ethylene bromide forms **Diphenylamidine-thioethylene**, which carbon disulphide converts into ethylene-phenyl-dithiocarbaminate (p. 615). These compounds contain the "five-membered" *thiazole* ring, hence they may be included among the thiazole (p. 554) derivatives (*Berichte*, 21, 1871).

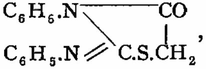


Chloracetic acid converts diphenylthiurea (*Annalen*, 207, 128) into:—

$$\left.\begin{array}{l}C_6H_5.NH\\ C_6H_5.N\end{array}\right\rangle C.S.CH_2.CO_2H$$

Diphenyl-thiohydantoïc Acid.

and



Diphenyl-thiohydantoïn.

the diphenyl derivatives of so-called thiohydantoïn and thiohydantoïc acid (p. 397).

Diphenylthiohydantoïn, $C_{15}H_{12}N_2SO$ (Diphenylamidine-thioglycollide), crystallizes from alcohol in leaflets, and melts at 176°. It decomposes, like the alkyl compounds (p. 617), when boiled with alcoholic potash, into diphenylurea, and thioglycollic acid, $HS.CH_2.CO_2H$. Boiling hydrochloric acid decomposes it into so-called glycolide of phenyl-mustard-oil, $C_6H_5.N\left\langle\begin{array}{l}CO\\ CO.S.CH_2\end{array}\right.$ (p. 616), and aniline.

Phenylthiohydantoïc Acid, $\left.\begin{array}{l}H_2N\\ C_6H_5.N\end{array}\right\rangle C.S.CH_2.CO_2H$ (Phenylamidine-thioglycollic acid), is produced (analogous to the formation of amidines from amines and cyanalkyls, p. 293) from aniline and sulphocyanacetic acid (or chlor-acetic acid and ammonium-sulphocyanate) (*Berichte*, 14, 732):—

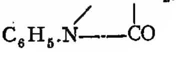
$$C_6H_5.NH_2 + CN.S.CH_2.CO_2H = C_6H_5.N{:}C\left\langle\begin{array}{l}NH_2\\ S.CH_2.CO_2H.\end{array}\right.$$

It is soluble in alcohol, crystallizes in needles, and melts at 148–152°. Boiling dilute sulphuric acid decomposes it into phenylurea and thioglycollic acid.

Isomeric, so-called (ortho)-**Phenylthiohydantoïc Acid**, $C_9H_{10}N_2SO_2$, is formed (analogous to thiohydantoïc acid (p. 397) from phenyl-thiourea and ammonium chlor-acetate (*Berichte*, 14, 1660):—

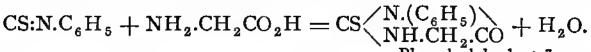
$$\left.\begin{array}{l}H_2N\\ C_6H_5.NH\end{array}\right\rangle CS + CH_2Cl.CO_2H = \left.\begin{array}{l}NH\\ C_6H_5.NH\end{array}\right\rangle C.S.CH_2CO_2H + HCl.$$

It is an amorphous mass, dissolving readily in alkalies and acids. The withdrawal of water from it yields so-called (ortho)-**Phenylthiohydantoïn**,



which melts at 178°, and is obtained from thio-urea and chloracet-anilide, $C_6H_5.NH.CO.CH_2Cl$. Boiling dilute hydrochloric acid converts it into the glycolide of phenyl-mustard oil (p. 616); ammonia is liberated simultaneously.

The real **Phenylsulphydantoïns**, corresponding to hydantoïn in constitution, and isomeric with the preceding so-called phenylthiohydantoïns (more correctly phenylamidine derivatives), are obtained by heating phenyl-mustard oil with glycocoll (amido-fatty acids) (*Berichte*, 17, 424):—



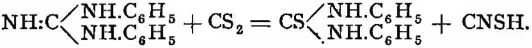
$$CS{:}N.C_6H_5 + NH_2.CH_2CO_2H = CS\left\langle\begin{matrix}N.(C_6H_5)\\NH.CH_2.CO\end{matrix}\right\rangle + H_2O.$$

Phenylsulphydantoïn.

They are converted into the corresponding phenylsulphydantoic acids on boiling with alcoholic potash, and are desulphurized by boiling with lead oxide.

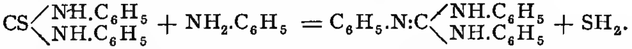
GUANIDINE DERIVATIVES (compare p. 294).

Diphenyl-guanidine, $HN{:}C\left\langle\begin{matrix}NH.C_6H_5\\NH.C_6H_5\end{matrix}\right.$ (Melaniline), is produced by the action of CNCl upon dry aniline, and by digesting cyananilide, $C_6H_5.NH.CN$, with aniline hydrochloride. It crystallizes in long needles, melting at 147°. It is a mono-acid base, forming crystalline salts. CS_2 transforms it into sulpho-carbanilide and sulphocyanic acid, which combines with a second molecule of diphenyl-guanidine:—



$$NH{:}C\left\langle\begin{matrix}NH.C_6H_5\\NH.C_6H_5\end{matrix}\right. + CS_2 = CS\left\langle\begin{matrix}NH.C_6H_5\\NH.C_6H_5\end{matrix}\right. + CNSH.$$

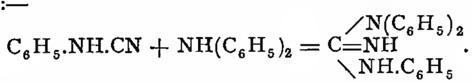
a-**Triphenyl-guanidine**, $C_6H_5.N{:}C\left\langle\begin{matrix}NH.C_6H_5\\NH.C_6H_5\end{matrix}\right.$, is obtained on heating diphenyl-urea and diphenyl-thiurea, alone or with reduced copper, to 140°. It is most readily prepared by digesting diphenyl-thiurea and aniline, with litharge or mercuric oxide (or by boiling with an iodine solution):—



$$CS\left\langle\begin{matrix}NH.C_6H_5\\NH.C_6H_5\end{matrix}\right. + NH_2.C_6H_5 = C_6H_5.N{:}C\left\langle\begin{matrix}NH.C_6H_5\\NH.C_6H_5\end{matrix}\right. + SH_2.$$

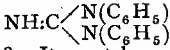
Triphenyl-guanidine crystallizes in rhombic prisms, melts at 143°, and is insoluble in water, sparingly soluble in ether, but readily in alcohol. It is a monacid base, and yields well crystallized salts. Heated with CS_2, it reverts again to diphenyl-thiurea and phenyl mustard oil.

Isomeric *β*-**Triphenyl-guanidine** is obtained by heating cyananilide with HCl-diphenylamine:—



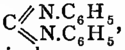
$$C_6H_5.NH.CN + NH(C_6H_5)_2 = C\begin{matrix}\diagup N(C_6H_5)_2\\=NH\\\diagdown NH.C_6H_5\end{matrix}.$$

It crystallizes in large plates, melting at 131° (see *Annalen*, 192, 9). It decomposes into diphenylamine, phenyl mustard-oil, and sulphocyanic acid when heated with carbon disulphide.

Symmetrical Tetraphenyl-guanidine,  $NH{:}C\begin{smallmatrix}N(C_6H_5)_2\\N(C_6H_5)_2\end{smallmatrix}$, is produced by the action of CNCl upon diphenylamine at 170°. Its crystals are insoluble in water, and melt at 130°.

CYANAMIDE DERIVATIVES (p. 289).

Cyananilide, $C_6N_6.NH.CN$, phenyl cyanamide (p. 289), is formed on conducting CNCl into a cooled ethereal solution of aniline, and by digesting phenylthiurea with litharge, or by heating it with lead acetate and alkali (*Berichte*, 18, 3220). It is readily soluble in alcohol and ether, but dissolves with difficulty in water. It contains ½ molecule of water of crystallization. It forms needles, melting at 47°. When allowed to stand in a desiccator, it loses water, becomes liquid, and in the air reverts to the crystalline hydrate. When heated it polymerizes to *Triphenyl-isomelamine*. It forms phenyl-thiurea with H_2S.

Carbodiphenylimide,  $C\begin{smallmatrix}N.C_6H_5\\N.C_6H_5\end{smallmatrix}$, is produced by the action of mercuric oxide upon diphenyl-thiurea in benzene solution, when H_2S is directly withdrawn (p. 616); or by the distillation of α-triphenyl-guanidine, when aniline separates. It is a thick liquid, boiling at 330°. It polymerizes upon standing, yielding a porcelanous mass, melting at 170°. When it absorbs water (boiling with alcohol), it yields diphenyl urea. It combines with H_2S to diphenyl thiurea, and with aniline to α-triphenyl-guanidine. It forms very stable bases with orthophenylenediamine, $C_6H_4(NH_2)_2$ (*Berichte*, 22, 3186).

Cyanuramide or Melamine Derivatives (p. 290).

Normal **Triphenylmelamine**, $C_3N_3(NH.C_6H_5)_3$, is produced in the action of cyanuric chloride on aniline, or by heating ethyl trithiocyanuric ester with aniline (p. 290) to 250–300° (*Berichte*, 18, 3218):—

$$C_3N_3(S.CH_3)_3 + 3NH_2.C_6H_5 = C_3N_3(NH.C_6H_5)_3 + 3CH_3.SH.$$

It consists of colorless needles, melting at 228°. Heated with hydrochloric acid to 150°, it breaks up into aniline and cyanuric acid.

Hexaphenylmelamine, $C_3N_3[N(C_6H_5)_2]_3$, melts at 300° and splits up into aniline and diphenylamine when heated to 200° with hydrochloric acid. It is formed by letting cyanuric chloride act upon diphenylamine.

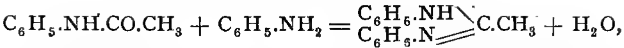
Triphenylisomelamine, $C_3N_3(C_6H_5)_3(NH)_3$. On long standing, phenylcyanamide polymerizes to this compound. Heating will effect the same. Or, it is produced when cyanogen bromide acts on aniline. It crystallizes in thick needles and melts at 185°. It dissolves in hydrochloric acid and forms double salts with $AuCl_3$ and $PtCl_4$. On warming with hydrochloric acid, it successively loses its NH-groups, oxygen entering, and the sole product is the triphenyl ester of isocyanuric acid (p. 613) (*Berichte*, 18, 3225). In addition to the normal triphenylmelamine and triphenylisomelamine, asymmetrical triphenylamines are known (*Berichte*, 18, 3226; 23, 1678).

Amidine derivatives (p. 293 and Benzenyl amidines).

In addition to the methods mentioned (p. 293), we can also produce the phenylated amidines by permitting PCl_3 or HCl to act upon a mixture of aniline with acid anilides:—

$$C_6H_5.NH.CHO + C_6H_5.NH_2 = \begin{smallmatrix}C_6H_5.NH\\C_6H_5.N\end{smallmatrix}\!\!>\!CH + H_2O,$$

Formanilide. Diphenyl-methenyl-amidine.



$$C_6H_5.NH.CO.CH_3 + C_6H_5.NH_2 = \begin{matrix} C_6H_6.NH \\ C_6H_5.N \end{matrix}\!\!>\!C.CH_3 + H_2O,$$

Acetanilide. Diphenyl-ethenyl-amidine.

or by conducting HCl into anilides, or by heating the same with HCl-salts of the anilines (*Berichte*, 15, 208 and 2449). They are feeble bases, and yield salts with 1 equivalent of hydrochloric acid. When boiled with aniline they are separated into aniline and acid anilides.

Diphenyl-methenyl-amidine (Methenyldiphenyl-diamine) results upon heating aniline with chloroform or formic acid to 180°, and by boiling phenyl-isocyanide, $C_6H_5.NC$, with aniline. It crystallizes from alcohol in long needles, melts at 135° and distils at 250°, with partial decomposition into $C_6H_5.NC$ and aniline.

Diphenyl-ethenyl-amidine melts at 131°.

Phenyl-ethenyl-amidine, $C_6H_5N{:}C(NH_2).CH_3$, from acetonitrile and HCl-aniline (p. 293), is a liquid.

We can also include here the so-called anhydro- and aldehydine bases (p. 628), which are obtained from the phenylenediamines of the ortho- series (see also Benzenyl-amidine).

PHOSPHORUS COMPOUNDS.

There is a series of phosphorus compounds corresponding to the benzene amido-derivatives.

Phenylphosphine, $C_6H_5.PH_2$, phosphaniline, is obtained by the action of hydriodic acid upon phosphenyl-chloride, $C_6H_6.PCl_2$. It is a liquid, boiling at 160° in a current of hydrogen, and possessing an extremely disagreeable odor. It sinks in water and is insoluble in acids. When exposed to the air it oxidizes to phosphenyl oxide, $C_6H_6.PH_2O$,—a crystalline mass easily soluble in water. Phenylphosphine combines with HI to the iodide, $C_6H_5.PH_3I$, out of which water again separates phenylphosphine.

Phosphenyl Chloride, $C_6H_5.PCl_2$, is formed by conducting a mixture of benzene and PCl_3 vapors through tubes heated to redness, by heating mercury diphenyl with PCl_3, and by the action of $AlCl_3$ upon benzene and PCl_3. It is a strongly refracting liquid, which fumes in the air, boils at 222°, and has a specific gravity 1.319 at 20°. It forms the *tetrachloride*, $C_6H_5.PCl_4$, with chlorine; this melts at 73°. With oxygen it yields the *oxychloride*, $C_6H_5.PCl_2O$, boiling at 260°. When the dichloride is heated with water we obtain phenyl-hypo-phosphorous acid, $C_6H_5.PHO.OH$ (melting at 70°), while the tetrachloride forms phenylphosphinic acid, $C_6H_5.PO.(OH)_2$, which melts at 158° (p. 155).

Phosphenyl chloride converts phenylphosphine into **Phospho-benzene**, $C_6H_5.P{:}P.C_6H_5$, corresponding to azobenzene, $C_6H_5.N{:}N.C_6H_5$.

Diphenylphosphine, $(C_6H_5)_2PH$, is obtained from diphenylphosphorchloride. It is an oil, boiling at 280° (*Berichte*, 21, 1507). *Diphenylphosphorchloride*, $(C_6H_5)_2PCl$, from mercury diphenyl, and phosphenyl-chloride, boils at 320° (*Berichte*, 18, 2108).

Triphenylphosphine, $(C_6H_5)_3P$, is produced from $C_6H_6.PCl_2$, and brombenzene, or from PCl_3 and brombenzene by the action of sodium (*Berichte*, 18, Ref. 562); it crystallizes in large plates, melts at 75° and boils at 360°.

Triphenylphosphine readily enters into compounds of pentavalent phosphorus (p. 169). It forms, with bromine, the dibromide, $(C_6H_5)_3PBr_2$, which is converted by water or alkalies into the dihydroxide, $(C_6H_5)_3P(OH)_2$. At 100° this passes into the oxide, $(C_6H_5)_3PO$. The latter melts at 153° and boils above 360°.

Triphenylphosphine and sulphur unite to the sulphide, $(C_6H_6)_3PS$, and with the alkyl iodides to phosphonium iodides, like $(C_6H_5)_3P.CH_3I$ (*Berichte*, 18, 562).

Phenoxyldiphenylphosphine, $(C_6H_5)_2P.O.C_6H_5$, is isomeric with triphenyl phosphine oxide. It is produced by the action of phenol upon diphenyl phosphor-chloride (see above): $(C_6H_5)_3\overset{V}{P}O$, isomeric with $(C_6H_5)_2\overset{III}{P}.O.C_6H_6$. This isomerism proves the *pentavalence of phosphorus* in the compounds PX_5 (*Berichte*, 18, 2118).

Toluene, xylene, and naphthalene form similar phosphorus derivatives. Analogous arsenic compounds exist. Furthermore, analogous arsenic (*Berichte*, 19, 1031) and antimony compounds, *e.g.*, Triphenylstibine, are known (*Berichte*, 18, Ref. 444).

Phenyl-silico-chloride, $C_6H_5.SiCl_3$, is prepared by heating mercury diphenyl and $SiCl_4$ to 300°. It is a liquid which fumes in the air and boils at 197°. Water decomposes it into the compound, $C_6H_5.SiO.OH$, which may be considered as benzoic acid in which the 1 carbon is replaced by silicon, hence it is called silico-benzoic acid. Alcohol forms the triethyl ether, $C_6H_5.Si(O.C_2H_5)_3$, boiling at 237°. Zinc-ethyl converts the chloride into *triethyl-phenyl-silicide*, $C_6H_5.Si.(C_2H_5)_3$, boiling at 230°.

Tetraphenyl Silicon, $Si(C_6H_5)_4$, is produced by the action of sodium upon a mixture of $SiCl_4$, chlorbenzene and ether (*Berichte* 18, 1540; 19, 1012). It is a white powder, which separates in a crystalline form from benzene. It melts at 228° and distils beyond 300°.

The arsenic and silicon compounds constitute the transition to the metallo-organic derivatives (p. 177); those containing tin, bismuth, mercury and lead are known in the benzene series.

Mercury-Phenyl $(C_6H_5)_2Hg$, is formed by treating brombenzene in benzene solution, for some time, with liquid sodium amalgam; the addition of some acetic ether facilitates the reaction (p. 181). It crystallizes in colorless rhombic prisms, melts at 120°, and can be sublimed. It assumes a yellow color in sunlight. It dissolves readily in benzene and carbon disulphide, but with more difficulty in ether and alcohol; in water it is insoluble. When distilled it decomposes for the most part into diphenyl, benzene and mercury. Acids decompose it with formation of benzene and mercury salts. Haloid compounds, *e.g.*, $C_6H_5.HgI$, are produced by the action of the halogens. Moist silver oxide converts them into hydroxyl derivatives, *e.g.*, $C_6H_5.Hg.OH$—a crystalline, very alkaline body, which separates ammonia from ammonium salts.

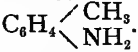
Bismuth-Triphenyl, $(C_6H_5)_3Bi$, is prepared by heating brombenzene and bismuth-sodium. It crystallizes, from hot alcohol, in needles or leaflets and melts at 82° (*Berichte*, 20, 54). When digested with concentrated hydrochloric acid it breaks up into bismuth-trichloride and benzene.

Tin-Tetraphenyl, $Sn(C_6H_5)_4$, may be produced by the action of tin-sodium (25% Na) upon brombenzene. It crystallizes in colorless prisms, melting at 226°. It sublimes and boils above 420° (*Berichte*, 22, 2917).

Lead-Tetraphenyl, $(C_6H_5)_4Pb$, is formed by heating brombenzene with lead-sodium and acetic ether. It is very much like the mercury-phenyl. It crystallizes in minute needles, melting at 225°, and decomposes above 270° (*Berichte*, 20, 717).

ANILINE HOMOLOGUES.

The aniline homologues, like aniline, are obtained by the reduction of the nitro-derivatives of the homologous benzenes. Technically, the methylated homologues (toluidine, xylidene, cumidine) are prepared by heating dimethylaniline or methyltoluidine hydrochlorides to 300° (p. 594).


$C_6H_4\begin{cases}CH_3\\NH_2\end{cases}$

Toluidines, $C_6H_4\langle{}^{CH_3}_{NH_2}$. The three isomerides are formed by the reduction of the three corresponding nitrotoluenes. Crude, commercial toluidine (p. 590), obtained by reducing common nitrotoluene, consists of solid para- and liquid ortho-toluidine; the former crystallizes out from the mixture.

To separate orthotoluidine from any para that continues in solution, the two are converted into acetyl compounds by digesting them with glacial acetic acid; in this new form they are dissolved in 4 parts concentrated acetic acid, and 80 parts of water are then added. The acetparatoluidine is precipitated, while the ortho-body continues in solution. Technically, they are separated from each other (and from aniline) by the different behavior of their HCl-salts toward sodium phosphate (*Berichte*, 19, 1718, 2728).

The following mixtures are handled in commerce: Aniline oil for *blue*, consisting of pure aniline; aniline oil for *red*, consisting of aniline, *o*-toluidine and *p*-toluidine in almost molecular quantities, and aniline oil for *saffron*, obtained from the distillate of the fuchsine fusion (échappês), is a mixture of aniline and *o*-toluidine.

When the toluidines are directly oxidized they behave like the anilines and usually change to azo-compounds; should the amido-group, however, contain acid radicals, these acid toluides can be oxidized by potassium permanganate, and by saponification yield amido-benzoic acids. Furthermore, the acid-toluides can be chlorinated, brominated, and nitrated the same as the anilides. The substituting negative group always arranges itself near the amido-group (in the ortho- position). Substituted toluidines are obtained by the saponification of these toluides.

Paratoluidine (1, 4), from solid paranitrotoluene, crystallizes in large plates, melts at 45°, and boils at 198°. It separates from boiling water, on cooling, in hydrous crystals, that sublime on exposure to the air. Bleaching lime does not color it. The acetyl compound, $C_7H_7.NH.C_2H_3O$, melts at 147°, and boils near 306°. Formyl toluide, $C_7H_7.NH.CHO$, is produced by distilling toluidine with oxalic acid (p. 606); when distilled with concentrated hydrochloric acid it yields (1, 4)-tolunitrile, which passes into terephthalic acid.

Methyl- and di-methyl-paratoluidine boil at 208°.

Upon heating *p*-toluidine with sulphur we obtain both thiotoluidine and dehydrothiotoluidine, $C_{14}H_{12}N_2S$—the parent substance of the *primulines* (see thiotoluidine and *Berichte*, 22, 581, 969).

Nitrosotoluidines, $C_7H_6(NO).NH_2$, may be prepared from the nitrosocresols by heating them with ammonium chloride and ammonium acetate (p. 599) (*Berichte*, 21, 729).

Orthotoluidine (1, 2) (Pseudotoluidine) does not solidify at —20°, and boils at 199°; its specific gravity at 16° is 1.00. Bleaching lime and hydrochloric acid color it violet, while a mixture of sulphuric and nitric acids gives it a blue color. Ferric chloride precipitates a blue compound (toluidine blue) from its hydrochloric acid solution. Its acet-compound melts at 107° and when oxidized with potassium permanganate and saponified yields ortho-amido benzoic acid (*Berichte*, 14, 263). It forms four isomeric nitro-orthotoluidines (*Annalen*, 228, 240) by the entrance of NO_2.

Metatoluidine (1, 3), from metanitrotoluene (*Berichte*, 22, 840) and metanitrobenzaldehyde (*Berichte*, 15, 2009), does not solidify at —13°, has a specific gravity of 0.998 at 25°, and boils at 202°. Its acetyl compound melts at 65°.

Ditolylamine, $(C_6H_4.CH_3)_2NH$, is produced like diphenylamine (p. 603) by heating HCl-toluidine with toluidine. It is a crystalline compound, boiling near 360°.

Xylidines, $C_6H_3(CH_3)_2.NH_2$.

The six possible isomerides are known. Three are derived from metaxylene, two from orthoxylene, and one from paraxylene (*Berichte*, 18, 2669). The commercial xylidine, obtained from dimethylaniline, serves for the preparation of red azo-dyestuffs, and consists chiefly of *amido-paraxylene* (*Berichte*, 18, 2664) and amido-metaxylene (*Berichte*, 18, 2919).

Amidotrimethyl-benzenes, $C_6H_2(CH_3)_3.NH_2$. The commercial product is made by heating xylidine hydrochloride with methyl alcohol to 256° under pressure; it serves for the preparation of red azo-dyestuffs and contains cumidine and mesidine (*Berichte*, 15, 1011, 2895). *Cumidine* is *Pseudocumidine* of the structure (1, 2, 4, 5—NH_2 in 1) (*Berichte*, 18, 92 and 1146); it consists mainly of nitropseudocumene; it melts at 63°, boils at 235°, and forms a nitrate that dissolves with difficulty. Pseudocumene, $C_6H_3(CH_3)_3$ (1, 3, 4), is produced by boiling its hydrazine compound, $C_6H_2(CH_3)_3.NH.NH_2$, with copper sulphate (see p. 633). Durylic acid is obtained by replacing the amido-group by bromine, and this by CO_2H. *Mesidine*, amido-mesitylene, is obtained from nitro-mesitylene, and boils at 227° (*Berichte*, 18, 2229).

Amido-Isodurene, $C_6H(CH_3)_4.NH_2$, is produced by heating pseudocumidine hydrochloride or mesidine hydrochloride with methyl alcohol. It boils at 250°. The replacement of its amido group by hydroxyl yields a tetramethylphenol, melting at 81° (*Berichte*, 18, 1149).

Amido-pentamethyl Benzene, $C_6(CH_3)_5.NH_2$, is very readily made by heating pseudocumidine and methyl iodide to 250° (*Berichte*, 18, 1821). It melts at 152° and boils at 277°. The replacement of its amido group gives rise to pentamethyl phenol, $C_6(CH_3)_5.OH$.

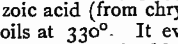
Homologues of aniline with higher alkyls are easily obtained on heating aniline with fatty alcohols and $ZnCl_2$ to 270–280° (p. 599); the alkyl assumes the para-position with reference to the amido group. *p*-**Amidoethylbenzene**, $C_6H_4(C_2H_5).NH_2$, also obtained from nitroethyl benzene (*Berichte*, 17, 767, 2800), boils at 214°. **Amidopropylbenzene**, $C_6H_4(C_3H_7).NH_2$, boils at 225°, the isopropyl compound at 217° (*Berichte*, 17, 1231) (see *Berichte*, 21, 1157). **Amidoisobutylbenzene**, $C_6H_4(C_4H_9).NH_2$, is easily obtained by heating aniline hydrochloride to 230° with isobutyl alcohol (*Berichte*, 18, 1009), and boils at 231°. **Amido-octyl Benzene**, $C_6H_4(C_8H_{17})NH_2$, from normal octyl alcohol, melts at 19°, and boils at 310° (*Berichte*, 18, 133).

DIAMIDO COMPOUNDS.

The **diamidobenzenes** or **phenylene-diamines**, $C_6H_4(NH_2)_2$, are formed by the reduction of the three dinitrobenzenes or nitroanilines (p. 598) with tin and hydrochloric acid; they can be obtained, also, from the six diamidobenzoic acids, $C_6H_3(NH_2)_2.CO_2H$, by the loss of carbon dioxide. They are also produced by the reduction of the nitroso compounds of the tertiary anilines, *e.g.*, $NO.C_6H_4.N(CH_3)_2$ (p. 598). The monamines can be converted into the diamines by first changing them to amido-azo-compounds, and then decomposing the latter by reduction (p. 645).

The diamines are colorless solids, but on exposure to the air they become colored. They are di-acid bases, forming well-defined salts. Ferric chloride imparts an intense red color to their solution.

Diamidobenzenes or Phenylenediamines, $C_6H_4(NH_2)_2$.

o-Diamidobenzene (1, 2), four-sided plates, melts at 102° and boils at 252°. Ferric chloride imparts a dark red color to its HCl-solution. When *o*-diamidobenzene (*o*-phenylene diamine) is shaken with benzoyl chloride and caustic soda the *dibenzoyl* derivative is formed—$C_6H_4.(NH.CO.C_6H_5)_2$ (p. 312 and *Berichte*, 21, 2744). *Diacyl* derivatives of the *o*-diamines are easily formed by heating with acid anhydrides (*Berichte*, 23, 1876), whereas if the free acids are employed ethenyl amidines are produced (p. 628). *m-Phenylenediamine* (1, 3), readily obtained from common dinitrobenzene, melts at 63° and boils at 287°. Very dilute nitrous acid solutions are colored intensely yellow by it; it can therefore be employed for the quantitative estimation of the former in aqueous solution (*Berichte*, 14, 1015). It combines with carbon disulphide to produce a peculiar compound, $C_6H_4(NH)_2CS$ (*Berichte*, 21, Ref. 521). *p-Phenylenediamine* (1, 4) melts at 147° and boils at 267°. Manganese peroxide and sulphuric acid convert it into quinone on boiling. If allowed to stand exposed to the air it oxidizes to green-red crystals, $C_6H_8N_2$ (*Berichte*, 22, Ref. 404). Its *dimethyl* compound,  $C_6H_3\begin{cases}N(CH_3)_2\\NH_2\end{cases}$, has already been described as *p*-amido-dimethylaniline (p. 601.) The tetramethyl derivative serves as a reagent for ozone (*Berichte*, 19, 3196).

Diphenylated diamidobenzenes, $C_6H_4(NH.C_6H_5)_2$, are produced by heating resorcinol and hydroquinone, $C_6H_4(OH)_2$, with aniline and $CaCl_2$ or $ZnCl_2$ (see dioxydiphenylamine, p. 604).

Triamidobenzenes, $C_6H_3(NH_2)_3$. The *adjacent* (1, 2, 3) is obtained from triamidobenzoic acid (from chrysanisic acid). When pure it is colorless, melts at 103° and boils at 330°. It even reduces silver solutions in the cold, is colored violet then brown by ferric chloride, and dissolves in sulphuric acid, containing a little nitric acid, with a deep blue color. The *unsymmetrical* (1, 2, 4) is obtained by the reduction of *a*-dinitroaniline (p. 598), and by the decomposition of chrysoïdine (*Berichte*, 15, 2197); it forms a crystalline mass and is colored a wine red by ferric chloride (*Berichte*, 17, Ref. 285). When oxidized by air, it changes to a eurhodine dyestuff (*Berichte*, 22, 856).

Tetra-amido benzenes, $C_6H_2(NH_2)_4$. The *symmetrical* (1, 2, 4, 5) variety is formed by the reduction of dinitro-*m*-phenylenediamine. It oxidizes very rapidly when liberated from its salts. It contains two amido-groups in the ortho- and para-positions, hence it exhibits all the reactions of the ortho- and para-diamines (see below) (*Berichte*, 22, 440). The *adjacent* (1, 2, 3, 4) variety, produced by the reduction of diquinoyl-tetroxime, $C_6H_2(N.OH)_4$, is also quite easily oxidized, and reacts like an orthodiamine (*Berichte*, 22, 1649).

Penta-amido benzene, $C_6H(NH_2)_5$, from trinitro-diamine, is very unstable on exposure to the air (*Berichte*, 21, 1547).

Diamidotoluenes, Toluylene-diamines, $C_6H_3(CH_3)(NH_2)_2$. *o-p-Diamidotoluene* (1, 2, 4—CH_3 in 1), obtained by the reduction of dinitrotoluene, consists of long needles, sparingly soluble in cold water, fusing at 99° and boiling at 280°. It is used in the preparation of toluylene red.

m-p-Diamidotoluene (1, 3, 4—CH_3 in 1), with the $2NH_2$-groups in the ortho-position, is obtained from nitroparatoluidine, forms scales that dissolve easily in cold water, melt at 89° and boil at 265°. Of the ortho-diamines, this one is most readily prepared. *o-m-Diamido-toluene* (1, 2, 3) (the two amido-groups are in the ortho-positions) is obtained from the corresponding nitroorthotoluidine. It melts at 62° and distils at 255° (*Annalen*, 228, 343). *o-o-Diamidotoluene* (1, 2, 6), from *o*-nitroorthotoluidine, melts at 103°.

Differences between the ortho-, meta- and para-diamines.—The three isomeric diamines differ markedly in numerous reactions, and the ortho-derivatives especially are characterized by their capability of forming various condensation products.

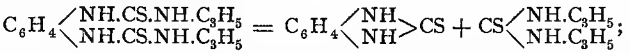
(1) The paradiamines, when digested in the warm with ferric chloride, are oxidized to quinones, *e.g.*, $C_6H_4O_2$, readily recognized by their odor. The same reagent precipitates from the orthodiamines (their salts) intensely colored compounds of complex constitution. Thus, orthophenylenediamine yields the ruby red compound, $C_{24}H_{18}N_6O.2HCl$ (*Berichte*, 17, Ref. 431).

(2) Nitrous acid (or $NaNO_2$) converts the *para*-diamines (their salts) into diazo-compounds, *e.g.*, $C_6H_4\begin{matrix}\diagup N_2X\\ \diagdown N_2X\end{matrix}$; the *meta*-diamines, on the contrary (as one NH_2 group is diazotized and two molecules unite), yield yellow brown azo-dyes, of the type of phenylene brown. The same products result from the action of the diazo-chlorides (see chrysoïdine) upon the meta-diamines. In very acid solution, and when there is a constant excess of acid (nitrous) the meta-diamines are also capable of forming diazo derivatives (*Berichte*, 19, 317). The *ortho*-diamines, when acted upon by the nitrous acid, yield *azimido*-compounds, *e.g.*, **Azimidobenzene**.

(3) When the hydrochlorides of the three isomerides are digested with ammonium sulphocyanide, disulphocyanides, like $C_6H_4\begin{matrix}\diagup NH_2.HSCN\\ \diagdown NH_2.HSCN\end{matrix}$, are produced. On heating these to 120°, we discover that the orthodiamines are changed to *phenylene sulphureas*, $C_6H_4\begin{matrix}\diagup NH\\ \diagdown NH\end{matrix}\!>\!CS$. These are not altered by digestion with an alkaline lead-solution (not desulphurized); while the derivatives, obtained from the *meta-* and *para*-diamines are immediately blackened by the alkaline lead solution (Reaction of Lellmann, *Berichte*, 18, Ref. 326). All diamines unite in a similar manner with the *mustard oils*, to form phenylene disulphalkylureas (see p. 389):—

$$C_6H_4(NH_2)_2 + 2CS{:}N.C_3H_5 = C_6H_4\begin{matrix}\diagup NH.CS.NH.C_3H_5.\\ \diagdown NH.CS.NH.C_3H_5.\end{matrix}$$

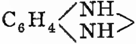
If these products be fused, those from the *ortho-diamines* decompose into *o*-phenylenesulphurea and dialkylsulphureas:—



$$C_6H_4\left\langle\begin{matrix}NH.CS.NH.C_3H_5\\ NH.CS.NH.C_3H_5\end{matrix}\right. = C_6H_4\left\langle\begin{matrix}NH\\ NH\end{matrix}\right\rangle CS + CS\left\langle\begin{matrix}NH.C_3H_5\\ NH.C_3H_5\end{matrix}\right.;$$

the fused mass instantly becomes crystalline, and the resulting phenylenesulphurea is not turned black by alkaline lead solutions. The *meta*-diamine derivatives melt with decomposition, while those of the *para*-, after fusion, are completely broken up (*Berichte*, 18, Ref. 327, and 19, 808).

The ortho-phenylene diamines yield peculiar bases by their union with carbodiphenylimide (p. 620). With phosgene they form **phenylene ureas**, *e.g.*,



$C_6H_4\left\langle\begin{matrix}NH\\ NH\end{matrix}\right\rangle CO$ (*Berichte*, 23, 1097).

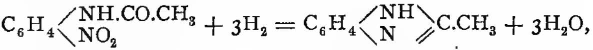
The para-diamines are also capable of yielding various dyestuffs. Mixed with primary amines (or phenols) and oxidized at the ordinary temperature, they are converted into *indoamine* and *indophenol* dyestuffs; at higher temperatures, the so-called *safranines* are produced. When oxidized with ferric chloride in the presence of H_2S, all the para-diamines, containing a free NH_2-group yield sulphurized dyes of thio-diphenylamine (Lauth's Dyestuffs, p. 605).

With the diazo-compounds, the meta-diamines form azo-colors (see above) while quinoxaline and phenazine colors are obtained from the ortho diamines by the action of ortho-diketones, etc.

Condensation Products of the Orthodiamines.—The ortho-diamines, in which the $2NH_2$-groups occupy the ortho-position, are capable of forming peculiar compounds, in which the two nitrogen atoms of the amido-groups are joined by one or two carbon atoms. They belong partly to the quinoxalines and partly to the phenazines. Analogous amidines are obtained from the amidophenols and amidothiophenols (see those of the ortho-series).

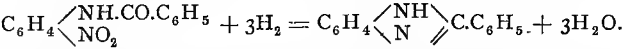
Amidine derivatives, or *anhydrobases* of the ortho-diamines are obtained:—

(1) By reducing the ortho-nitro acid anilides with tin and hydrochloric or acetic acid, the NO_2-groups being converted into NH_2 and water eliminated at the same time—*Anhydrobases*, of Hobrecker and Hübner (*Annalen*, 209, 339):—



$$C_6H_4\left\langle\begin{matrix}NH.CO.CH_3\\ NO_2\end{matrix}\right. + 3H_2 = C_6H_4\left\langle\begin{matrix}NH\\ N\end{matrix}\right\rangle C.CH_3 + 3H_2O,$$

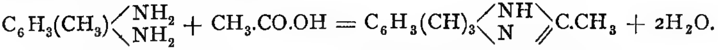
Ortho-nitro-acetanilide. Ethenyl-phenylene-amidine.



$$C_6H_4\left\langle\begin{matrix}NH.CO.C_6H_5\\ NO_2\end{matrix}\right. + 3H_2 = C_6H_4\left\langle\begin{matrix}NH\\ N\end{matrix}\right\rangle C.C_6H_5 + 3H_2O.$$

o-Nitro-benzanilide. Benzenyl-phenylene-amidine.

(2) The same anhydrobases, or amidines, are directly produced from the orthodiamines on heating them with acids (*e.g.*, formic acid, acetic acid, benzoic acid, phthalic acid); the acid anilides formed at first (*Berichte*, 19, 1757), lose water (*Berichte*, 8, 677; 10, 1123):—

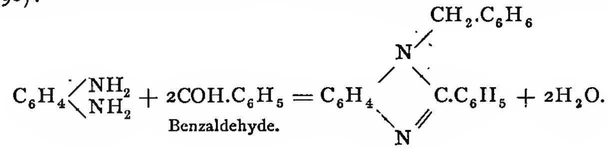


$$C_6H_3(CH_3)\left\langle\begin{matrix}NH_2\\ NH_2\end{matrix}\right. + CH_3.CO.OH = C_6H_3(CH)_3\left\langle\begin{matrix}NH\\ N\end{matrix}\right\rangle C.CH_3 + 2H_2O.$$

o-Toluylene Diamine. Toluylene-Ethenyl Amidine.

The same products result on heating the ortho-diamines with acetoacetic ester (*Berichte*, 19, 2977; 12, 953); paraphenylene diamine, on the other hand, forms an anilide of aceto-acetic acid (*Berichte*, 19, 3303).

(3) The ortho-diamines yield similar derivatives with the aldehydes (benzaldehyde, furfurol, salicylic aldehyde)—**Aldehydine bases** of Ladenburg (*Berichte*, 11, 590):—



$$C_6H_4\left\langle\begin{matrix}NH_2\\NH_2\end{matrix}\right. + 2COH.C_6H_5 = C_6H_4\left\langle\begin{matrix}N(CH_2.C_6H_6)\\N\end{matrix}\right\rangle C.C_6H_5 + 2H_2O.$$

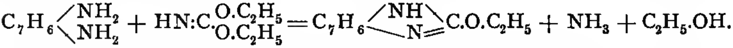
If the hydrochloric acid salts of the diamines (with 2HCl) be employed in this reaction, one molecule of hydrochloric acid is set free, and the ortho-diamines can thereby be readily distinguished from the meta- and para-diamines (*Berichte*, 11, 1650).

The latest investigations prove the *aldehydine bases to be real amidines*, inasmuch as benzaldehydine can also be prepared from benzenyl-phenylene amidine (see above) by heating with benzyl chloride, $C_6H_5.CH_2Cl$ (*Berichte*, 19, 2025). The fatty aldehydes are also capable of yielding analogous aldehydine bases (*Berichte*, 20, 1585).

Condensation products are obtained when the *free* diamines act upon aldehydes (*Berichte*, 22, 2724).

The phenyleneamidines (anhydrobases and aldehydines) are perfectly analogous to the diphenylene amidines (p. 620). These are crystalline and very stable compounds. Being monacid bases, they generally form well crystallized salts. They do not unite with acid chlorides or anhydrides. They combine with the alkyl-iodides (1 and 2 molecules) to ammonium iodides, yielding corresponding hydroxides with caustic potash.

Phenylene-methenyl Amidine, $C_6H_4\left\langle\begin{matrix}NH\\N\end{matrix}\right\rangle CH$, phenylene-formamidine, (p. 293), from *o*-phenylene diamine and formic acid, melts at 167°. **Phenylene-ethenyl Amidine,** $C_6H_4\left\langle\begin{matrix}NH\\N\end{matrix}\right\rangle C.CH_3$, phenylene-acetamidine, melts at 176°. **Phenylene benzamidine,** $C_9H_4\left\langle\begin{matrix}NH\\N\end{matrix}\right\rangle C.C_6H_5$, melts at 280°. Benzaldehydine results upon heating it with benzyl chloride (see above). An oxy-derivative of methenyl amidine is produced on heating *o*-toluylene diamine with imidocarbonic ester (p. 384):—

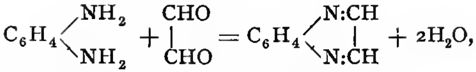


$$C_7H_6\left\langle\begin{matrix}NH_2\\NH_2\end{matrix}\right. + HN:C\begin{matrix}O.C_2H_5\\O.C_2H_5\end{matrix} = C_7H_6\left\langle\begin{matrix}NH\\N\end{matrix}\right\rangle C.O.C_2H_5 + NH_3 + C_2H_5.OH.$$

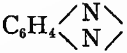
On heating the ethenyl-compound with hydrochloric acid, we get

Toluylene-oxy-methenyl amidine, or Toluylene Urea, $C_7H_6\left\langle\begin{matrix}NH\\N\end{matrix}\right\rangle C.OH$, or $C_7H_6\left\langle\begin{matrix}NH\\NH\end{matrix}\right\rangle CO$ (tautomeric forms), which can also be formed by heating *o*-toluylene-diamine with urea (*Berichte*, 19, 2652). *o*-Phenylene-sulphurea, $C_6H_4\left\langle\begin{matrix}NH\\NH\end{matrix}\right\rangle CS$ (p. 627), is analogous to *o*-toluylene-urea.

A very interesting condensation of the ortho-diamines is that with glyoxal, CHO.CHO and other dicarbonyl derivatives, —.CO.CO.—, when they form basic compounds of the quinoxaline type:



$$C_6H_4\begin{matrix}\diagup NH_2\\ \diagdown NH_2\end{matrix} + \begin{matrix}CHO\\ |\\ CHO\end{matrix} = C_6H_4\begin{matrix}\diagup N{:}CH\\ |\\ \diagdown N{:}CH\end{matrix} + 2H_2O,$$

and also of that of *phenazine*,  $C_6H_4\begin{matrix}\diagup N \diagdown\\ \diagdown N \diagup\end{matrix}C_6H_4$ (see these).

Upon this behavior Hinsberg and Körner have based the reaction for the detection of the ortho-diamines by means of phenanthraquinone. A more delicate test is obtained by using croconic acid (*Berichte*, 19, 2727).

The ortho-diamines unite with grape-sugar (*Berichte*, **20**, 281 and 495).

DIAZO-COMPOUNDS.

The amido-group is directly replaced by hydroxyl, when nitrous acid acts upon the primary amido-derivatives of the marsh-gas series (p. 161):—

$$R.NH_2 + NO_2H = R.OH + N_2 + H_2O.$$

The benzene amido products, on the other hand, first yield intermediate compounds—the so-called diazo-compounds—which can be further transformed into hydroxyl derivatives:—

$$\underset{\text{Amido-benzene.}}{C_6H_5.NH_2.} \qquad \underset{\text{Diazo-benzene Nitrate.}}{C_6H_5.N_2.NO_3.} \qquad \underset{\text{Phenol.}}{C_6H_6.OH.}$$

We obtain either diazo- or diazo-amido compounds, according to the conditions of the reaction. If nitrous acid (or its vapors) be permitted to act on the salts of amido-derivatives in aqueous solution, salts of the diazo-compounds are formed:—

$$\underset{\text{Aniline Nitrate.}}{C_6H_5.NH_2NO_3H} + NO_2H = \underset{\text{Diazo-benzene Nitrate.}}{C_6H_5.N_2.NO_3} + 2H_2O.$$

If, however, we act on the *free* amido-derivatives, in alcoholic or ethereal solution, *diazo-amido-compounds* result:—

$$2C_6H_5.NH_2 + NO_2H = \underset{\text{Diazo-amido-benzene.}}{C_6H_5.N_2.NH.C_6H_5} + 2H_2O.$$

The diazo compounds are produced at first, but they then combine with a second molecule of the free base and form diazo-amido-derivatives (p. 631):—

$$C_6H_5.N_2.NO_3 + C_6H_5.NH_2 = C_6H_5.N_2.NH.C_6H_5 + NO_3H.$$

Instead of using free nitrous acid (its vapors) with amido-salts, we can obtain the diazo-derivatives more easily and in purer form, by dissolving the amido-compounds in two equivalents of dilute nitric or sulphuric acid, and then adding an equivalent amount of potassium or sodium nitrite to the solution (*Berichte*, 8, 1073):—

$$C_6H_5.NH_2.NO_3H + NO_3H + NO_2K = C_6H_5.N_2.NO_3 + 2H_2O + NO_3K.$$

To obtain the diazoamido-compounds add amyl nitrite or ethyl nitrite (1 molecule) to the ethereal solution of the amido-derivative (2 molecules) and allow the latter to evaporate over sulphuric acid (*ibid*):—

$$2C_6H_5.NH_2. + C_2H_5.O.NO = C_6H_5.N_2.NH.C_6H_5 + H_2O + C_2H_5.OH.$$

They are more easily prepared by adding the aqueous solution of NO_2K and KOH (1 molecule each) to the aqueous solution of the HCl-anilines (2 molecules):—

$$2C_6H_5.NH_2.HCl + NO_2K + KOH = C_6H_5.N_2.NH.C_6H_5 + 2KCl + 3H_2O.$$

It is frequently recommended to substitute sodium acetate for alkalies (*Berichte*, 17, 641). In this case the reaction proceeds so that the diazo-compound is formed by NO_2K and 1 molecule of $C_6H_5.NH_2.HCl$, and this immediately combines with the aniline liberated by the KOH and forms the diazo-amido-product (see amido-azo-benzene). All the above reactions must be executed in the cold.

Nitrous acid converts the secondary aniline bases into the same diazo-compounds, the alkyl group disappearing as alcohol:—

$$C_6H_5.NH(C_2H_5).NO_3H + NO_2H = C_6H_5.N_2.NO_3 + H_2O + C_2H_5.OH;$$

whereas nitroso-compounds result if potassium nitrite be employed (p. 600).

Further action of nitrous acid on the dissolved diazoamido-derivatives transforms them into diazo-compounds, and the latter, finally, by action of water, into phenols.

Another procedure, occasionally applicable in diazotizing, consists in letting zinc dust and hydrochloric acid act upon the nitrate of the diazo-derivative (Möhlau):—

$$C_6H_5.NH_2.NO_3H + Zn + 3HCl = C_6H_5.N_2Cl + ZnCl_2 + 3H_2O.$$

P. Griess first discovered the diazo-compounds early in the '60's; their constitution was explained by Kekulé. They all contain the diazo-group of two nitrogen atoms, which on the one side replaces an atom of hydrogen in benzene, and on the other is attached to a monovalent group, as seen in the following formulas:—

Diazobenzene nitrate,	$C_6H_5.N{=}N.O.NO_2$
" sulphate,	$C_6H_5.N{=}N.O.SO_3H$
" chloride,	$C_6H_5.N{=}NCl$
Potassium diazobenzene,	$C_6H_5.N{=}N.OK$
Silver "	$C_6H_5.N{=}N.OAg$
Diazo-amidobenzene,	$C_6H_5.N{=}N.NH.C_6H_5$
Diazo-benzene sulphonate,	$C_6H_5.N{=}N.SO_3H.$

The structure of the diazo-compounds is now fully proved by the existence of the so-called tetrabrombenzene-diazosulphonic acid, $C_6Br_4\left\langle{N_2 \atop SO_2}\right\rangle$ (*Berichte*, 9, 1537), and also by their relations to the hydrazines (*Annalen*, 190, 100).

Free diazo-benzene has not been as yet prepared pure, nor analyzed; it, however, corresponds to the formula, $C_6H_5.N{=}N.OH$.

The diazo-chlorides form double salts with auric and platinic chlorides, *e. g.*:—

$$C_6H_5.N_2Cl.AuCl_3 \qquad (C_6H_5.N_2Cl)_2.PtCl_4.$$

The diazobromides also combine with two additional atoms of bromine, yielding *perbromides* :—

$C_6H_5.N_2Br.Br_2$, Diazobenzene Perbromide.

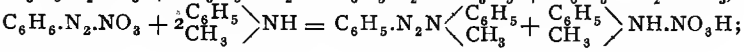
Potassium sulphite converts the sulphates into *diazosulphonic acids* :—

$$C_6H_5.N_2.SO_4H + SO_3K_2 = C_6H_5.N_2.SO_3K + SO_4KH.$$

These pass into hydrazines when reduced.

The **Diazoamido-compounds** are also produced by the direct action of salts of the diazo-derivatives upon primary and secondary anilines (*Berichte*, **14**, 2448) :—

$$C_6H_5.N_2.NO_3 + 2C_6H_5.NH_2 = C_6H_5.N_2.NH.C_6H_5 + C_6H_5.NH_2.HNO_3,$$



$$C_6H_6.N_2.NO_3 + 2\left.\begin{matrix}C_6H_5\\CH_3\end{matrix}\right>NH = C_6H_5.N_2N\left<\begin{matrix}C_6H_5\\CH_3\end{matrix}\right. + \left.\begin{matrix}C_6H_5\\CH_3\end{matrix}\right>NH.NO_3H;$$

also :—

$$C_6H_5.N_2.OK + C_6H_5.NH_2.HCl = C_6H_5.N_2.NH.C_6H_5 + KCl + H_2O.$$

This explains their formation by the action of nitrous acid upon the free amido-compounds (p. 630). See p. 638 for the constitution of the diazo-amido-compounds of substituted anilines.

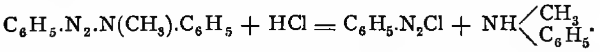
They can also be obtained by the action of the nitroso-amines upon the primary amido-bodies :—

$$(C_6H_5)_2N.NO + NH_2.C_6H_5 = (C_6H_5)_2.N.N:N.C_6H_5 + H_2O.$$

It is not only with the primary and secondary anilines, but also with the primary and secondary (not tertiary) amines of the fatty series, with which the diazo-compounds are capable of combining, thus forming *mixed* diazoamido compounds, *e. g.* :—

$C_6H_5.N_2.NH.C_2H_5$ and $C_6H_5.N_2.N(CH_3)_2$.

When sodium alcoholate and alkyl iodides act upon the diazo-amido derivatives the hydrogen of the NH-group is easily replaced by the alkyls. An excess of cold hydrochloric acid will reduce the resulting diazo-alkylamido-compounds into diazochlorides and alkyl anilines :—



$$C_6H_5.N_2.N(CH_3).C_6H_5 + HCl = C_6H_5.N_2Cl + NH\left<\begin{matrix}CH_3\\C_6H_5\end{matrix}\right..$$

This is a proof of the accepted constitution of the diazoamido derivatives (*Berichte*, **19**, 2034, 3239).

The salts of the diazo-compounds are mostly crystalline, colorless bodies, which speedily brown on exposure to the air. They are readily soluble in water, slightly in alcohol, and are precipitated from the latter solution by ether. They are generally very unstable, and decompose with a violent explosion when they are heated, or struck a blow.

The diazo-salts are first obtained in solution, from which it is rather troublesome to get them in a solid form (p. 636). They can be obtained as solids by applying the aniline salts in alcoholic solution and acting upon the same with amyl nitrite (*Berichte*, 23, 2995).

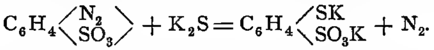
The diazo-derivatives are very reactive, and enter numerous, readily occurring reactions, in which nitrogen is liberated, and the diazo-group in the benzene nucleus directly replaced by halogens, hydrogen, hydroxyl, and other groups.

(1) When the salts (sulphates are best) are boiled with water, the diazo-group is replaced by hydroxyl and phenols are produced:—

$$C_6H_5.N_2.NO_3 + H_2O = C_6H_6.OH + N_2 + NO_3H,$$
$$C_6H_5.N_2.Br + H_2O = C_6H_5.OH + N_2 + HBr.$$

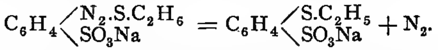
Mononitrophenols result upon digesting in the warm with 1 molecule of nitric acid (*Berichte*, 18, 1338). See *Berichte*, 20, 1137, for abnormal transpositions.

The substitution of the diazo-group by the sulphydrate group (SH) occurs upon digesting diazo-benzenesulphonic acid with alcoholic potassium sulphide (*Berichte*, 20, 350):—



$$C_6H_4\left\langle\begin{matrix}N_2\\SO_3\end{matrix}\right\rangle + K_2S = C_6H_4\left\langle\begin{matrix}SK\\SO_3K\end{matrix}\right. + N_2.$$

In the same manner, when mercaptan acts upon diazobenzenesulphonic acid, a compound results, which, upon standing or warming, liberates N_2, and is transposed into the ethyl sulphid-derivative (*Berichte*, 17, 2075):—



$$C_6H_4\left\langle\begin{matrix}N_2.S.C_2H_6\\SO_3Na\end{matrix}\right. = C_6H_4\left\langle\begin{matrix}S.C_2H_5\\SO_3Na\end{matrix}\right. + N_2.$$

(2) If alcohol be employed instead of water, then hydrogen will enter for the diazo-group, and hydrocarbons result. The alcohol is oxidized to aldehyde:—

$$C_6H_6.N_2.HSO_4 + C_2H_6O = C_6H_6 + N_2 + SO_4H_2 + C_2H_4O.$$

Instead of first converting the amido- into the diazo-compounds, we can directly substitute H for NH_2, by adding their compounds to alcohol saturated with N_2O_3 (ethyl nitrite), and then applying heat. In this way diazo-derivatives appear at first, but they are at once decomposed by the alcohol. Sometimes it is advisable to dissolve the amido-derivatives in a little concentrated sulphuric acid, lead nitrous acid into the solution, and then decompose with alcohol (*Berichte*, 9, 899). It has occurred upon boiling with alcohol that the diazo-group was not replaced by hydrogen but by oxy-ethyl ($O.C_2H_5$); this was the case in slight degree with aniline and toluidine (*Berichte*, 17, 1917; 18, 65). If the dry diazo salt be decomposed with alcohol, phenol ethers are the chief products (*Berichte*, 21, Ref. 96; 22, Ref. 657).

The replacement of the diazo-group by hydrogen is sometimes effected by its conversion into the hydrazine derivative and then boiling this with copper sulphate or ferric chloride (see phenyl hydrazine). The reaction taking place on boiling the diazo-chlorides with a stannous chloride solution, is, in all probability, dependent upon the intermediate formation of hydrazines (*Berichte*, 17, Ref. 741):

$$C_6H_4(C_4H_9).N_2Cl + SnCl_2 + H_2O = C_6H_5(C_4H_9) + N_2 + SnOCl_2 + HCl.$$

An analogous procedure for the replacement of the diazo-group by hydrogen consists in dissolving the diazo-compound in caustic soda and adding a solution of stannous oxide in sodium hydroxide (*Berichte*, 22, 587).

(3) Chlorbenzenes are formed, if the $PtCl_4$-double salts (p. 630) are heated alone, or, what is better, with dry soda or salt:—

$$(C_6H_5.N_2Cl)_2.PtCl_4 = 2C_6H_5Cl + N_2 + 2Cl_2 + Pt.$$

When the diazo-perbromides are subjected to dry distillation, or boiled with alcohol (the latter is oxidized to aldehyde), brombenzenes are formed:—

$$C_6H_5.N_2.Br_3 = C_6H_5Br + N_2 + Br_2.$$

On digesting the diazo-salts with hydriodic acid, iodobenzenes separate:—

$$C_6H_5.N_2.SO_4H + HI = C_6H_5I + N_2 + SO_4H_2.$$

HBr and HCl react similarly, providing the diazo-compounds contain additional negative groups (*Berichte*, 8, 1428, and 13, 964).

The diazo-group in the three diazocinnamic acids can be replaced by chlorine on boiling with concentrated HCl-acid (*Berichte*, 16, 2036).

The dry sulphates of the diazo-benzoic acids deport themselves in a similar manner when heated with the concentrated haloid acids (*Berichte*, 18, 961).

In addition to phenols, large quantities of chlor- and brom-benzenes are produced on boiling the benzene diazochlorides with hydrochloric or hydrobromic acid (*Berichte*, 18, 337, 1936).

(4) Remarkable transpositions of the diazo salts have been effected through the agency of cuprous compounds (Reactions of Sandmeyer).

Chlorbenzenes result upon heating diazo-chlorides, in aqueous solution, with a solution of cuprous chloride. At first compounds, containing cuprous chloride, are produced (*Berichte*, 19, 810), but these rapidly undergo further decomposition:—

$$C_6H_5.N_2Cl.Cu_2Cl_2 = C_6H_5Cl + N_2 + Cu_2Cl_2.$$

The yield is greater, if the solution of the diazo-chloride be allowed to gradually run into the boiling HCl-solution of cuprous chloride (*Berichte*, 17, 1633; 23, 1880). Or cuprous chloride is added to the HCl-solution of the amide, the liquid then heated to boiling, and sodium nitrite added (*Berichte*, 17, 2651). In this way amidophenols yield chlorphenols, and phenylenediamines yield dichlorbenzenes. By adding potassium bromide, the diazo-group is replaced by bromine and bromphenols are formed. Sandmeyer's method is especially adapted for the formation of chlorine and bromine derivatives. The fluorine and iodine derivatives are better prepared from diazo-amido compounds (*Berichte*, 21, Ref. 97).

The diazo-group can be replaced by the nitro-group, forming nitro-benzenes. This may be accomplished by adding the diazobenzene nitrite solution to freshly precipitated cuprous oxide (*Berichte*, **20**, 1495; **23**, 1630):—

$$C_6H_5.N_2.NO_2 = C_6H_5(NO_2) + N_2.$$

If copper sulphate be mixed with potassium cyanide, and the diazochloride solution added to it, the diazo-group will be displaced by the cyanogen group and nitriles will result:—

$$C_6H_5.N_2Cl + CNK = C_6H_5.CN + N_2 + KCl.$$

Thus the three isomeric nitroanilines, $C_6H_4<^{NH_2}_{NO_2}$, yield three nitrocyanides, $C_6H_4<^{CN}_{NO_2}$, which can be further converted into the three nitrobenzoic acids, $C_6H_4(NO_2).CO_2H$. Likewise, the three amido-benzoic acids, $C_6H_4<^{CO_2H}_{NH_2}$, can be transformed into the three phthalic acids, $C_6H_4(CO_2H)_2$ (*Berichte*, **18**, 1492). Thus aniline yields nitrobenzene (*Berichte*, **20**, 1495).

Sulphocyanides (*Rhodanides*) result when the diazo-salts are boiled with potassium and cuprous sulphocyanides (*Berichte*, **23**, 738, 770):—

$$C_6H_5.N_2Cl + CN.SK = C_6H_5.SCN + N_2 + KCl.$$

A modification in Sandmeyer's method, which frequently is of practical advantage, consists in using *reduced copper*, as a substitute for cuprous chloride (Gattermann, *Berichte*, **23**, 1219; compare *Berichte*, **23**, 1881). In this way it is also possible to introduce the group N:CO thus forming *phenylisocyanates*, if a potassium cyanate solution and copper powder be added to the diazo-salt (*Berichte*, **23**, 1223):—

$$C_6H_5.N_2Cl + CNOK = C_6H_5.N{:}CO + N_2 + KCl.$$

If copper powder or zinc dust acts upon diazo-benzene sulphate diphenyl results (*Berichte*, **23**, 1227). Upon boiling diazo-benzene sulphonic acids with copper powder and formic acid hydrogen replaces the diazo-group and benzene sulphonic acids are formed (*Berichte*, **23**, 1632).

The *diazo-amido-compounds*, *e. g.*, $C_6H_5.N_2.NH.C_6H_5$, diazoamidobenzenes, are generally yellow-colored, neutral bodies which do not combine with acids. They are insoluble in water, but dissolve in alcohol, ether and benzene. As a general thing they are more stable than the diazo-compounds, and do not often change color on exposure to air; yet they undergo reactions analogous to those of the diazo-derivatives. In so doing they are resolved into their components: the amido-compound breaks off, while the diazo-group sustains the corresponding transformation:—

$$C_6H_5.N_2.NH.C_6H_5 + 2HBr = C_6H_5Br + N_2 + C_6H_5.NH_2.HBr,$$
$$C_6H_5.N_2.NH.C_6H_5 + H_2O = C_6H_5.OH + N_2 + C_6H_5.NH_2.$$

Phenol and aniline are also produced by boiling with concentrated hydrochloric acid. By using cold, concentrated hydrochloric acid the immediate action is the decomposition into diazo-chloride and aniline. The reaction is especially adapted to the formation of fluorine derivatives (p. 583).

Nitrous acid converts the amido- into the diazo-group:—

$$C_6H_5.N_2.NH.C_6H_5 + NO_2H + 2NO_3H = 2C_6H_5.N_2.NO_3 + 2H_2O.$$

On boiling the alcoholic solution with sulphurous acid, the diazo-group is replaced by the sulpho-group, with formation of benzene-sulphonic acids (*Berichte*, 9, 1715):—

$$C_6H_5.N_2.NH.C_6H_5 + 2SO_3H_2 = C_6H_5.SO_3H + N_2 + NH_2.C_6H_5.SO_3H_2.$$

The diazo-derivatives of the substituted amides react similarly. Therefore the conversion through the diazo- or diazoamido-compounds is an excellent means of transforming amido-derivatives (and also nitro-) into the corresponding halogen- and oxy-compounds. Thus, we successively obtain from the three isomeric nitranilines the following derivatives belonging to the three series:—

$$C_6H_4\left\{\begin{matrix}NO_2\\NH_2\end{matrix}\right. \quad C_6H_4\left\{\begin{matrix}NO_2\\N_2X\end{matrix}\right. \quad C_6H_4\left\{\begin{matrix}NO_2\\Br\end{matrix}\right. \text{ or } C_6H_4\left\{\begin{matrix}NO_2\\OH\end{matrix}\right.;\text{ and}$$

$$C_6H_4\left\{\begin{matrix}NH_2\\Br\end{matrix}\right. \quad C_6H_4\left\{\begin{matrix}N_2.X\\Br\end{matrix}\right. \quad C_6H_4\left\{\begin{matrix}Br\\Br\end{matrix}\right. \text{ or } C_6H_4\left\{\begin{matrix}OH\\OH\end{matrix}\right..$$

Conversion of Diazo- into Azo-Compounds.—Besides the changes described the diazo-compounds exhibit other noteworthy reactions. While they form diazo-amido-derivatives with primary and secondary anilines (p. 631), they yield amido-azo-derivatives with tertiary anilines (p. 642), as the diazo-group encroaches upon a new benzene nucleus:—

$$C_6H_5.N_2.NO_3 + C_6H_5.N(CH_3)_2 = \underset{\text{Dimethylamido-azobenzene.}}{C_6H_5.N_2.C_6H_4.N(CH_3)_2} + NO_3H.$$

They act in the same manner on the phenols, the phenolsulphonic acids and phenylenediamines, $C_6H_4(NH_2)_2$, of the meta-series, producing various classes of coloring substances (the chrysoïdines and tropæolines), which belong to the group of azo-compounds (p. 640).

In an analogous manner, the diazo-amido compounds are transposed into azo-derivatives by simply standing, or through the action of anilines (p. 642):—

$$\underset{\text{Diazoamido-benzene.}}{C_6H_5.N_2.NH.C_6H_5} \text{ yields } \underset{\text{Amido-azo-benzene.}}{C_6H_6.N_2.C_6H_4.NH_2}.$$

For the relations of the diazo- to the hydrazine derivatives, see latter.

Reactions of the Diazo-Compounds.—All, even the diazo-amido-compounds, give intense colorations (reaction of Liebermann), if added to a mixture of phenol and concentrated sulphuric acid. The nitroso-compounds (and also the nitrites) do the same. When an alcoholic solution of meta-diamido-benzene (or other meta-diamido derivatives) is added to a similar solution of the diazo-derivatives, red or brown colorations result; the diazoamido-bodies react under these conditions only after the addition of acetic acid (*Berichte*, 9, 1309). The resulting azo-derivatives belong to the chrysoïdines (p. 643).

Diazobenzene Nitrate, $C_6H_5.N_2.NO_3$, is formed by the action of nitrous acid upon an aqueous or alcoholic solution of aniline nitrate, or upon an ethereal solution of diazo-amidobenzene (in presence of nitric acid).

Preparation.—Pour a little water over the aniline nitrate. Cool the flask with ice from the outside and conduct in nitrous acid (from As_2O_3 and HNO_3, specific gravity 1.35 (see *Berichte*, 18, Ref. 116) until all the substance has dissolved and potassium hydroxide, added to a small portion of the mixture, does not separate aniline. The dark solution is then filtered and alcohol and ether added, when diazobenzene nitrate is precipitated as a crystalline mass. Or, potassium nitrite may be allowed to act upon aniline nitrate (p. 629). The solid salt is more easily obtained by using alcohol and amyl nitrite (p. 632).

Diazobenzene nitrate forms long, colorless needles, and when dry is rather stable. It browns in moist air and decomposes rapidly. When heated it explodes with violence.

Diazobenzene sulphate, $C_6H_5.N_2.SO_4H$, is similarly obtained from aniline sulphate. It is advisable to add sulphuric acid (diluted with 2 volumes of water), alcohol (3 volumes) and then ether to the solution of diazobenzene nitrate. The sulphate then separates out at the bottom of the aqueous solution. After a second treatment with alcohol and ether, and evaporation under an air pump, it can be obtained crystalline. It consists of colorless needles or prisms, which dissolve readily in water. It explodes at 100°. It is, perhaps, also better in this case to use alcohol and amyl nitrite for the precipitation of the salt (p. 632).

Diazobenzene Sulphonic Acid, $C_6H_5.N_2.SO_3H$. Its potassium salt is obtained by adding diazobenzene nitrate to a cold, neutral or feebly alkaline solution of potassium sulphite. The liquid solidifies to a crystalline mass of $C_6H_5.N_2.SO_3K$ (*Annalen*, 190, 73). Acid potassium sulphite forms potassium benzene-hydrazine-sulphonate, $C_6H_5.N_2.H_2.SO_3K$.

Diazobenzene Bromide, $C_6H_5.N_2Br$, separates in white laminæ, if bromine be added to the ethereal solution of diazo-amido-benzene. Tribrom-aniline remains in solution. Ether precipitates the bromide from its alcoholic solution.

Diazobenzene Perbromide, $C_6H_5.N_2Br_3$, is precipitated from the aqueous solution of diazobenzene nitrate or sulphate, by bromine in HBr-acid or NaBr. It is a dark-brown oil, which quickly becomes crystalline. It is insoluble in water and ether, and crystallizes from cold alcohol in yellow laminæ. Continued washing with ether converts it into the diazo-bromide.

The *Platinum Double Salt*, $(C_6H_5.N_2Cl)_2.PtCl_4$, is precipitated in yellow prisms on adding a hydrochloric acid solution of $PtCl_4$ to the solution of the nitrate or sulphate. It is slightly soluble in water, and deflagrates when heated.

Potassium Diazobenzene, $C_6H_5.N_2.OK$, is separated, as a yellow liquid, from diazobenzene nitrate, by concentrated caustic potash. It crystallizes when evaporated on the water-bath, forming white, pearly leaflets, which readily dissolve in water and alcohol; the aqueous solution decomposes quickly.

Silver Diazobenzene, $C_6H_6.N_2.OAg$, is precipitated as a gray compound from the potassium salt by silver nitrate. It explodes very violently.

The compounds with mercury, lead, zinc, and other metals, are formed in a similar manner.

Acetic acid liberates *diazobenzene* (p. 630) from the potassium salt in the form of a heavy oil. It decomposes at once.

Diazo-amido-benzene, $C_6H_5.N_2.NH.C_6H_5$ (p. 634), is obtained by the action of nitrous acid on the alcoholic solution of aniline; by mixing diazobenzene nitrate with aniline, and by pouring a slightly alkaline sodium nitrite solution upon aniline hydrochloride (p. 630).

Dissolve aniline in alcohol (6–10 volumes), cool and conduct nitrous acid into the solution until a portion crystallizes on evaporation. The solution is then poured into water. A dark oil separates and soon becomes crystalline. It is washed out with cold, and then crystallized from hot alcohol.

Another method consists in adding sodium-nitrite (1 molecule), and then sodium-acetate (*Berichte*, 17, 641; 20, 1581) to the hydrochloric acid (3 molecules) solution of aniline (2 molecules). Caustic soda forms amido-azobenzene at once. Or dissolve 50 parts of aniline in 15 parts of fuming sulphuric acid and 1500 parts of water. To this solution add sodium nitrite, when the temperature of the liquid is 25–30° (*Berichte*, 19, 1953).

Diazo-amidobenzene consists of golden-yellow, shining laminæ or prisms. It is insoluble in water, sparingly soluble in cold, but readily in hot alcohol, ether and benzene. It melts at 98°, and then explodes.

It does not combine with acids, although it forms a double salt $(C_{12}H_{11}N_3.HCl)_2.PtCl_4$, with hydrochloric acid and $PtCl_4$. It crystallizes in reddish needles. When the alcoholic solution is mixed with silver nitrate, the compound, $C_6H_5.N_2NAg.C_6H_5$, separates in reddish needles.

When the alcoholic solution stands, especially in the presence of a little aniline-hydrochloride, the diazo-amidobenzene sustains an interesting transposition, resulting in the production of amido-azobenzene (p. 641).

Substituted anilines, *e.g.*, $C_6H_4Br.NH_2$, act with nitrous acid just the same as aniline. They yield perfectly analogous diazo compounds.

Free *diazo-chlor-* and *diazo-brom-benzene*, $C_6H_4Br.N_2.OH$ (p. 630), are crystalline compounds. They have not been analyzed because of their instability. Higher substituted anilines, such as trinitro-aniline, $C_6H_2(NO_2)_3.NH_2$, cannot form diazo-derivatives.

The aniline homologues, toluidine, xylidine, yield perfectly analogous diazo- and diazo-amido-compounds with perfectly similar properties. Thus, the three toluidines (ortho-, meta- and para-) yield *three* corresponding isomeric *diazotoluidines*:—

$$C_6H_4(CH_3)NH_2 \quad \text{give} \quad C_6H_4(CH_3).N_2X.$$

The para-variety of the three *diazo-amido toluenes*, $C_6H_4(CH_3).N_2.N.C_6H_4.CH_3$, is alone stable. The ortho- and meta-forms (from ortho- and meta-toluidine) immediately pass into amido-azo-derivatives.

It is strange that the mixed diazo-amido-compounds, which, according to their mode of formation, should be different, are in fact identical. Thus, diazo-benzene-amido-brom-benzene, $C_6H_5.N_2.NH.C_6H_4Br$, from diazobenzene and brom-aniline, is identical with diazobrombenzene-amidobenzene, $C_6H_4Br.N_2.NH.C_6H_5$, from diazobrombenzene and aniline. The following are also identical:—

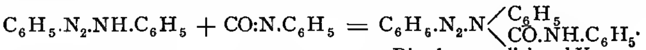
$C_6H_5.N_2.NH.C_6H_4.CH_3$ and $(CH_3)C_6H_4.N_2.NH.C_6H_5$.
Diazobenzene-amidotoluene. Diazotoluene-amidobenzene.

$C_6H_5.N_2.NH.C_6H_4.CO_2H$ and $(CO_2H)C_6H_4.N_2.NH.C_6H_5$.
Diazo-benzene-amidobenzoic Acid. Diazobenzoic acid-amido benzene.

This anomalous behavior can probably be accounted for by assuming that the isomeric formulas are tautomeric, the hydrogen atom oscillating from the imide- to the diazo-group (p. 54). Another conception allows but *one* of the formulas to the two compounds; according to this, the diazo-group and the amido-group transpose themselves, the former always, however, entering the para-position (*Berichte*, 19, 3239):—

$C_6H_5.N_2.NH.C_6H_4.CH_3$ (1, 4). yields $C_6H_5.NH.N_2.C_6H_4.CH_3$. (1, 4).
Diazobenzene-*p*-amido-toluene. Amidobenzene-*p*-diazo-toluene.

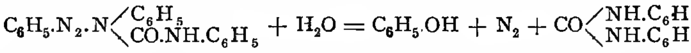
Experiments instituted to settle this question, have given contradictory results (*Berichte*, 20, 3004; 21, 1020). The results with phenyl-cyanate are probably more correct (p. 613). This reagent combines with the diazo-amido compounds, and yields diazo-benzene-diphenyl ureas:—



$$C_6H_5.N_2.NH.C_6H_5 + CO{:}N.C_6H_5 = C_6H_6.N_2.N\left\langle\begin{matrix}C_6H_5\\ CO.NH.C_6H_5\end{matrix}\right.$$

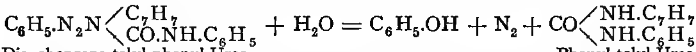
Diazobenzene-diphenyl Urea.

The latter decompose into diazobenzene (its decomposition products) and diphenyl ureas:—



$$C_6H_5.N_2.N\left\langle\begin{matrix}C_6H_5\\ CO.NH.C_6H_5\end{matrix}\right. + H_2O = C_6H_5.OH + N_2 + CO\left\langle\begin{matrix}NH.C_6H_5\\ NH.C_6H_5\end{matrix}\right.$$

The mixed diazo-amido compounds react similarly. The product obtained by the action of diazobenzene upon paratoluidine, and *p*-diazotoluene upon aniline, yields with phenylcyanate a compound that, on decomposing, forms phenyl-tolyl-urea. It is, therefore, diazobenzene-amido-toluene, $C_6H_5.N_2.NH.C_7H_7$. The decomposition of its phenylcyanate may be expressed as follows:—



$$C_6H_5.N_2N\left\langle\begin{matrix}C_7H_7\\ CO.NH.C_6H_5\end{matrix}\right. + H_2O = C_6H_5.OH + N_2 + CO\left\langle\begin{matrix}NH.C_7H_7\\ NH.C_6H_5\end{matrix}\right.$$

Diazobenzene-tolyl-phenyl Urea. Phenyl-tolyl Urea.

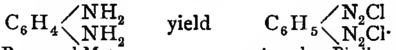
Other mixed diazo-amido-derivatives behave similarly. They are distinct bodies; in their formation a transposition occurs, in that the *imide group attaches itself to the more negative radical* (Goldschmidt, *Berichte*, 21, 1016; 22, 2578).

On mixing diazo-benzene salts with primary and secondary amines, the products are *mixed* diazo-amido compounds containing radicals of the paraffin series.

Diazobenzene-ethylamine, $C_6H_5.N_2.NH.C_2H_5$, and **Diazobenzene-dimethylamine**, $C_6H_6.N_2.N(CH_3)_2$, are yellow oils, that form very unstable salts with acids.

Bis-diazo-amido-derivatives are obtained by further action of diazobenzene salts upon the compounds with primary amines, *e. g.*, $(C_6H_5.N_2)_2N.CH_3$, bis-diazo-benzene-methylamine (*Berichte*, 22, 942).

Bisdiazo-compounds (p. 626) are formed from the diamines of the para- and meta-series:—



$$C_6H_4\left\langle\begin{matrix}NH_2\\NH_2\end{matrix}\right. \quad \text{yield} \quad C_6H_5\left\langle\begin{matrix}N_2Cl\\N_2Cl\end{matrix}\right.$$

Para- and Meta. *p*- and *m*-Bisdiazo-chlorides.

These are also termed *tetrazo*-compounds. The ortho-diamines, on the other hand, yield the azimido-derivatives (see below).

Diazimido- or Triazo-compounds, $C_6H_5.N_3$. These are derivatives of *azoimide*, $HN\left\langle\begin{matrix}N\\ \|\\ N\end{matrix}\right.$, recently discovered (*Berichte*, 23, 3023). They are produced:

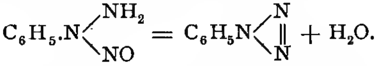
(1) By the action of aqueous ammonia upon diazobenzene perbromides:—

$$C_6H_5.N_2.Br_3 + 4NH_3 = C_6H_5.N_2.N + 3NH_4Br.$$

(2) By the action of hydroxylamine upon diazobenzene sulphate:—

$$C_6H_5.N_2.SO_4H + NH_2OH = C_6H_5.N_3 + H_2O + SO_4H_2;$$

and most readily and easily by the action of sodium nitrite upon the hydrochloric acid solution of phenylhydrazine, when the nitrosophenylhydrazine first produced sustains decomposition (Fischer, *Annalen*, 190, 92):—



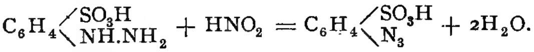
$$C_6H_5.N\left\langle\begin{matrix}NH_2\\NO\end{matrix}\right. = C_6H_5N\left\langle\begin{matrix}N\\ \|\\ N\end{matrix}\right. + H_2O.$$

Benzenediazimide.

Triazobenzenes, like *benzene-diazimide* or *triazo-benzene*, $C_6H_5.N_3$, are yellow oils, insoluble in water. Their odor is stupefying. They are volatile in a vacuum and in a current of steam. They explode at the ordinary pressure, if heated. They are decomposed into N_2 and chloranilines when boiled with hydrochloric acid (*Berichte*, 19, 313).

Substituted diazobenzenes yield analogous triazo-compounds. Thus, nitro-diazobenzene bromide, $C_6H_4(NO_2).N_2Br$, yields *amido-triazobenzene*, $C_6H_4\left\langle\begin{matrix}NH_2\\N_3\end{matrix}\right.$, which, by diazotizing, etc., forms *Bistriazobenzene*, $C_6H_4\left\langle\begin{matrix}N_3\\N_3\end{matrix}\right.$, or *Hexazobenzene.* White leaflets, melting at 83°. It explodes violently, if heated to a higher temperature (*Berichte*, 21, 1559).

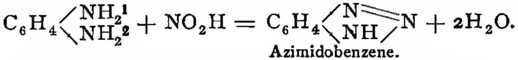
Nitrous acid converts hydrazobenzene sulphonic acid into *Triazobenzene sulphonic acid* (*Berichte*, 21, 3409):—



$$C_6H_4\left\langle\begin{matrix}SO_3H\\NH.NH_2\end{matrix}\right. + HNO_2 = C_6H_4\left\langle\begin{matrix}SO_3H\\N_3\end{matrix}\right. + 2H_2O.$$

Another peculiar formation is that of the triazo-compounds by the action of diazo-salts upon hydrazines (*Berichte*, 20, 1528; 21, 3415).

The *Azimido*-compounds are isomeric with the diazimido-derivatives. They are produced by the action of nitrous acid upon ortho-phenylene diamines:—



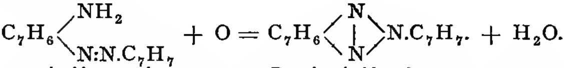
$$C_6H_4\langle{}^{NH_2^1}_{NH_2^2} + NO_2H = C_6H_4\langle{}^{N\equiv}_{NH}\rangle N + 2H_2O.$$

Azimidobenzene.

They behave like secondary bases; their imide hydrogen can be replaced by metals, acid radicals and alkyls. The alkyl derivatives can combine further with alkyl iodides and yield ammonium compounds (Zincke, *Berichte*, 22, Ref. 139; 23, Ref. 105).

Azimido benzene, $C_6H_4{:}N_3H$, isomeric with diazimido- or triazo-benzene, $C_6H_5.N_3$, forms white needles, melting at 98.5°.

Pseudo-azimides are intimately related to the azimido-derivatives. They are formed by oxidizing the ortho-amido-azo-compounds with chromic acid (*Berichte*, 23, 106, 1315, 1844):—



$$C_7H_6\langle{}^{NH_2}_{N:N.C_7H_7} + O = C_7H_6\langle{}^{N}_{N}\rangle N.C_7H_7. + H_2O.$$

o-Amido-azo-toluene. Pseudoazimido-toluene.

Benzoylazimide, $C_6H_5.CO.N_3$ (Triazobenzoyl), is formed by the action of nitrous acid upon benzoyl hydrazine, $C_6H_5.CO.NH.NH_2$. When decomposed, it yields benzoic acid and the remarkable compound known as

Azoimide, $HN{:}N_2$, *Hydrazoic Acid.* This is perfectly analogous to the haloid acids. It conducts itself similarly (Curtius, *Berichte*, 23, 3023).

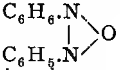
AZO-COMPOUNDS.

Like the diazo-derivatives, these contain a group, consisting of two nitrogen atoms; in the former the N_2-group is combined with only one benzene nucleus; here it is attached on either side to benzene nuclei:—

$C_6H_5N_2X.$ Diazo-compounds. $C_6H_5.N_2.C_6H_5.$ Azo-compounds.

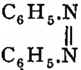
In consequence, they are far more stable than the former, and do not react with the elimination of nitrogen. They are classified as azoxy-, azo-, and hydrazo-compounds. They constitute, as it were, a transition from the nitro- to the amido-derivatives:—

$C_6H_6.NO_2.$ Nitrobenzene.



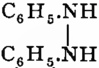
$$\begin{matrix} C_6H_6.N \\ | \\ C_6H_5.N \end{matrix}\rangle O$$

Azoxybenzene.



$$\begin{matrix} C_6H_5.N \\ \| \\ C_6H_5.N \end{matrix}$$

Azobenzene.



$$\begin{matrix} C_6H_5.NH \\ | \\ C_6H_5.NH \end{matrix}$$

Hydrazobenzene.

$C_6H_5.NH_2.$ Amidobenzene.

They are obtained according to the following methods:—

1. By *reduction* of the nitro-compounds in *alkaline* solution. Amido-derivatives are formed in acid solutions. By moderated reduction with an alcoholic potassium hydroxide solution (Zinin), or zinc dust and ammonia, *azoxy*-compounds are produced at first (the alcohol is oxidized to aldehyde):—

$$2C_6H_5.NO_2 = (C_6H_5)_2N_2O + 3O.$$

Stronger reducing agents (sodium amalgam in alcoholic solution, zinc dust with sodium hydroxide) immediately form the *azo-* and *hydrazo*-derivatives. In many cases the action of $SnCl_2$ in equivalent quantity, dissolved in NaOH (2 molecules $SnCl_2$ for 1 molecule of the nitro-compound), is well adapted for the preparation of the azo-compounds (Witt, *Berichte*, **18**, 2912). (All the nitrobenzene compounds, excepting nitronaphthalene, react similarly).

2. By the *oxidation* of the primary amido-derivatives in alkaline solution with potassium permanganate or potassium ferricyanide (*Berichte*, **9**, 2098). Energetic reducing agents convert all the azo-derivatives into amido-bodies (p. 645).

3. By the action of sodium or potassium upon primary amido-compounds. Sodium amido-derivatives result and the oxygen of the air oxidizes them to azo-derivatives (*Berichte*, **10**, 1802):—

$$2C_6H_5.NHK + O_2 = (C_6H_6)_2N_2 + 2KOH.$$

Similarly, bromaniline yields azobenzene, as the bromine is reduced by the nascent hydrogen. The action of $C_6H_5.NCl_2$ upon aniline produces azobenzene (*Berichte*, **16**, 1048).

4. By the action of the nitroso-compounds upon the primary amines (see Nitrosophenol):—

$$C_6H_5.NH_2 + ON.C_6H_4.OH = C_6H_5.N{:}N.C_6H_4.OH + H_2O.$$

Reducing agents (H_2S) also further change the azoxy- to azo- and hydrazo-compounds; conversely, when the hydrazo- are oxidized (even in the air) they become azo-compounds.

The azoxy- and azo-derivatives are solids with a yellow to brown color, and do not unite with acids; the hydrazo-bodies are colorless and when in alcoholic solution, are easily changed by acids to isomeric diamido-diphenyls. By the action of stannous chloride and a slight quantity of sulphuric acid upon the alcoholic solution of the azo-bodies, the latter can be directly converted into benzidines (*Berichte*, **19**, 2970). Because of their stability, the azo-compounds can be directly chlorinated, nitrated and sulphonated.

On reducing the nitro-azo-derivatives, we obtain the *amido-azo compounds*:—

$$\underset{\text{Nitro-azobenzene.}}{C_6H_5.N_2.C_6H_4.NO_2} \quad \text{yields} \quad \underset{\text{Amido-azobenzene.}}{C_6H_5.N_2.C_6H_4.NH_2.}$$

These are also obtained from the diazo-compounds by peculiar reactions:—

(1) By direct transposition of the diazoamido-compounds (p. 635):—

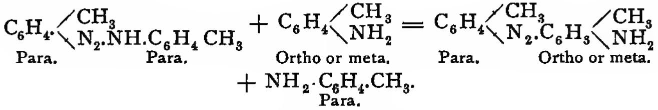
$$\underset{\text{Diazoamidobenzene.}}{C_6H_5.N_2.NH.C_6H_5} \quad \text{forms} \quad \underset{\text{Amido-azobenzene.}}{C_6H_5.N_2.C_6H_4.NH_2.}$$

In the case of diazoamido-benzene, this transposition occurs on standing with alcohol, but more readily by the action of a slight quantity of aniline hydrochloride (*Berichte*, 19, Ref. 24).

The group $NH.C_6H_5$ is eliminated from the diazo-compound, and the diazo-group, N_2, attaches itself to the benzene nucleus of the aniline:—

$$C_6H_5.N_2.NH.\underset{a}{C_6H_5} + \underset{b}{C_6H_5}.NH_2 = C_6H_5.N_2.\underset{b}{C_6H_4}.NH_2 + \underset{a}{C_6H_5}.NH_2.$$

As aniline is regenerated here, a very slight quantity of it suffices to transform the diazo- into the azo-compound. That the reaction indeed occurs as indicated, is verified by the knowledge that other (homologous) amido-compounds act similarly upon the diazo-amido-derivatives. Thus we obtain azo-derivatives from diazo-amido-toluene, by the action of the salts of meta- and ortho-toluidine (*Berichte*, 10, 664 and 1156):—



$$\underset{\text{Para.}}{C_6H_4}\left\langle\begin{matrix}CH_3\\ N_2.NH.\underset{\text{Para.}}{C_6H_4}CH_3\end{matrix}\right. + \underset{\text{Ortho or meta.}}{C_6H_4\left\langle\begin{matrix}CH_3\\ NH_2\end{matrix}\right.} = \underset{\text{Para.}}{C_6H_4}\left\langle\begin{matrix}CH_3\\ N_2.C_6H_3\left\langle\begin{matrix}CH_3\\ NH_2\end{matrix}\right.\end{matrix}\right. \underset{\text{Ortho or meta.}}{} + \underset{\text{Para.}}{NH_2.C_6H_4.CH_3.}$$

This would go to prove that the reaction only occurs readily, if in the reacting amido-compound the position in the benzene nucleus adjacent to the amido group in the para place be unoccupied; the diazo group, N_2, then arranges itself in the para-position referred to the NH_2 of the amido-compound.

This explains, too, why only diazoamido compounds are obtained from para-toluidine by nitrous acid, whereas the ortho- and meta-toluidines (in which the para-position is free) immediately yield the amido-azo derivatives (p. 638), because the diazoamido-bodies first produced can immediately transpose themselves. It was formerly thought, that in the production of azoamido-compounds, the diazo-group could invariably only enter the *para*-position (referred to the amido-group.) This, however, occurs only with special ease in alcoholic solution. On heating diazoamido-paratoluene, dissolved in fused paratoluidine, to 65° with paratoluidine hydrochloride, a transposition will also take place with formation of *ortho amido-azo-toluene*, $C_6H_4(CH_3).N_2.C_6H_3(CH_3).NH_2$ (melting at 118°), as the diazo-group enters the *ortho*-position (referred to amido group) (*Berichte*, 17, 77). The diazo compounds behave in a similar manner with phenols (p. 643).

Diazobenzene-ethylamine and dimethylamine (p. 638) react like the diazo-amido-compounds with aniline hydrochloride, the alkylamines breaking off at the same time:—

$$C_6H_5.N_2.N(CH_3)_2 + C_6H_5.NH_2 = C_6H_5.N_2.C_6H_4.NH_2 + NH(CH_3)_2.$$

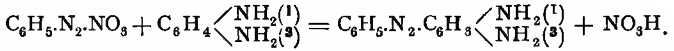
(2) By the action of the diazo-compounds upon the tertiary ani-

lines (diazoamido-derivatives first result from the primary and secondary anilines, p. 635):—

$$C_6H_6.N_2.NO_3 + C_6H_6.N(CH_3)_2 = C_6H_5.N_2.C_6H_4.N(CH_3)_2 + NO_3H.$$

In this reaction also, the N_2-group enters the position *para* with reference to the amido-group, and therefore dimethyl paratoluidine does not react (*Berichte*, 10, 526). Paradiazobenzene sulphonic acid acts directly on the HCl-anilines, forming sulpho-acids of the amidoazo-compounds (*Berichte*, 15, 2184).

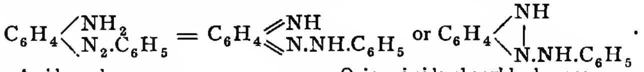
(3) By the action of the diazo-compounds upon the diamido-derivatives of the meta-series (p. 636), those of the ortho- and para-places not reacting (*Berichte*, **10**, 389 and 654):—



$$C_6H_5.N_2.NO_3 + C_6H_4\left<\begin{matrix}NH_2(1)\\NH_2(3)\end{matrix}\right. = C_6H_5.N_2.C_6H_3\left<\begin{matrix}NH_2(1)\\NH_2(3)\end{matrix}\right. + NO_3H.$$

The resulting compounds are dyestuffs, called *chrysoïdines* (p. 648), varying in color from orange to brown.

The most recent research would seem to indicate that the amido-azo-compounds of the ortho-series are quinone-derivatives (similar to the so-called nitrosophenols), and, indeed, *hydrazones* of *quinon-imides*. It is probably an instance of tautomerism of formulas (*Berichte*, 23, 497):—

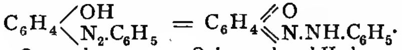


$$C_6H_4\left<\begin{matrix}NH_2\\N_2.C_6H_5\end{matrix}\right. = C_6H_4\left<\!\!\!\begin{matrix}\diagup\!\!\!\diagup NH\\ \diagdown\!\!\!\diagdown N.NH.C_6H_5\end{matrix}\right. \text{ or } C_6H_4\left<\begin{matrix}NH\\ |\\ N.NH.C_6H_5\end{matrix}\right..$$

o-Amido-azobenzene. *o*-Quinon-imide-phenyl-hydrazone.

Arguments favoring this view, are the production of pseudo-azimides by the oxidation of the *o*-amido-azo-benzenes (p. 640) and the reduction of the *o*-diazo-azo-benzenes to diazo-hydrides (*Berichte*, 20, 1176).

Probably, also, the oxy-azo-compounds of the ortho-series should be regarded as hydrazones of the quinones (*Berichte*, 22, 3234; 23, 487):—



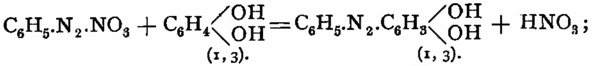
$$C_6H_4\left<\begin{matrix}OH\\N_2.C_6H_5\end{matrix}\right. = C_6H_4\left<\begin{matrix}\diagup\!\!\!\diagup O\\ \diagdown\!\!\!\diagdown N.NH.C_6H_5\end{matrix}\right..$$

o-Oxy-azobenzene. Quinone-phenyl Hydrazone.

The diazo-derivatives react analogously with the phenols, forming *oxyazo-compounds*. With the monovalent phenols we have:—

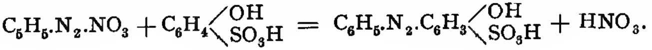
$$C_6H_5.N_2.NO_3 + C_6H_5.OH = C_6H_5.N_2.C_6H_4.OH + HNO_3;$$

with the divalent phenols of the *meta series* (as resorcinol):—



$$C_6H_5.N_2.NO_3 + \underset{(1,3).}{C_6H_4\left<\begin{matrix}OH\\OH\end{matrix}\right.} = C_6H_5.N_2.\underset{(1,3).}{C_6H_3\left<\begin{matrix}OH\\OH\end{matrix}\right.} + HNO_3;$$

and with phenol-sulphonic acids and amidophenols of the meta series:—

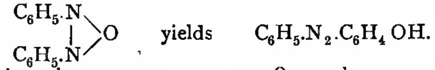


$$C_5H_5.N_2.NO_3 + C_6H_4\left<\begin{matrix}OH\\SO_3H\end{matrix}\right. = C_6H_5.N_2.C_6H_3\left<\begin{matrix}OH\\SO_3H\end{matrix}\right. + HNO_3.$$

They are also produced on heating the diazo-amido-benzenes with phenols, and with resorcinol (*Berichte*, 20, 372, 904 and 1577; **21**, 1112):—

$$C_6H_5.N_2.NH.C_6H_5 + C_6H_5.OH = C_6H_5.N_2.C_6H_4.OH + C_6H_5.NH_2.$$

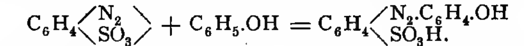
Or, by the molecular rearrangement induced by heating azoxybenzenes with sulphuric acid (see oxy-azo-benzene, p. 646):—



$$\left.\begin{array}{l} C_6H_5.N \\ \quad | \\ C_6H_5.N \end{array}\right\rangle O \quad \text{yields} \quad C_6H_5.N_2.C_6H_4\,OH.$$

Azoxy-benzene. Oxy-azo-benzene.

The *sulpho-acids* of the azo-compounds (see above) can also be prepared by heating the latter with concentrated or fuming sulphuric acid (by directly *sulphonating* them—see benzene sulphonic acid). An easier course consists in letting diazo compounds act upon phenol sulphonic or amido-sulphonic acids, or conversely by combining diazobenzene sulphonic acids and amines or phenols:—



$$C_6H_4\left\langle\begin{array}{l} N_2 \\ SO_3 \end{array}\right\rangle + C_6H_5.OH = C_6H_4\left\langle\begin{array}{l} N_2.C_6H_4.OH \\ SO_3H. \end{array}\right.$$

Diazobenzene Sulphonic Acid. Phenol. Oxy-azobenzene Sulphonic Acid.

These oxyazo- and amido-azo-sulphonic acids are called *tropæolines;* many of them are applied as dyestuffs.

The diazo-compounds act on the phenols in aqueous solution, but more readily when alkali is present (diazobenzene sulphate forms only phenyl ether or phenyl oxide, $(C_6H_5)_2O$, with aqueous phenol). Ordinarily the phenol derivative is dissolved in dilute alkalies and the aqueous diazo-chloride added. Occasionally it is advisable to apply sodium acetate instead of caustic alkalies (*Berichte*, 17, 641). Variations occur in the reaction sometimes, attributable to the quantity of alkali, whether it be in excess or in equivalent amount (*Berichte*, 17, 878). In the case of diazo-compounds and mono- and di-valent phenols two isomeric products, *a* and *β*, may arise—products soluble and insoluble in alkali (*Berichte*, 17, 877), (see Dibenzene-disazoresorcinol, p. 647).

As in the amido-compounds, so in the phenols, the entering diazo-group prefers and assumes the para position with reference to the hydroxyl group (p. 642); in the divalent phenols, like resorcinol, it takes the para-position referred to the *one* hydroxyl. When the *p*-position is occupied the diazo-group can assume the ortho-position, *e. g.*, in *p*-cresol, *p*-phenolsulphonic acid and *β*-naphthol (*Berichte*, 17, 876; 21, Ref. 814).

The amido-azo- and oxy-azo-compounds are yellow to brown in color, readily soluble in alcohol, and usually crystalline. The salts with acids and alkalies constitute what are known technically as azo-dyestuffs (p. 650). While the colored azo-compounds (having the *chromophorus* atomic group N=N) are not themselves dyes, they do acquire, by the entrance of the *chromogenic*, salt-forming groups OH and NH_2, the character of dyestuffs (Witt, *Berichte*, 9, 552). They are decolorized by reducing agents (tin and hydrochloric acid, zinc chloride, boiling with zinc dust, or upon digestion with ammonium sulphide), taking up four hydrogen atoms and being resolved into two amido-compounds. The azo-group, N=N, decomposes, each nitrogen atom remaining attached as NH_2 to a benzene nucleus:—

$$C_6H_5.N_2.C_6H_4NH_2 + 2H_2 = C_6H_5.NH_2 + C_6H_4(NH_2)_2.$$

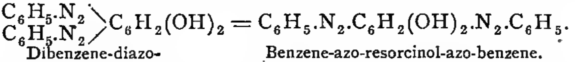
Thus, *p*-oxy-azobenzene is resolved into aniline and *p*-amidophenol. This reaction, therefore, may serve for the determination of the constitution of azo-compounds (*Berichte*, **21**, 3471). Such a decomposition occasionally takes place by heating with hydrochloric acid, indulines being simultaneously produced (*Berichte*, **17**, 395). Consult *Berichte*, **15**, 2812, upon the nomenclature of the azo-derivatives.

Nitrous acid converts the amido-azo-derivatives (like the amido-derivatives) into diazo-, *e. g.*, $C_6H_5.N_2.C_6H_4.N_2Cl$, azobenzene diazochloride, which, like simple diazo- and amido-derivatives, act on the phenols, forming so-called *tetrazo-compounds*, *e. g.*:—

$$C_6H_5.N_2.C_6H_4.N_2.C_6H_4.OH. \qquad C_6H_5.N_2.C_6H_4.N_2.C_6H_3(OH)_2.$$

Azobenzene-azo-phenol. Azobenzene-azo-resorcinol.

Such compounds can also be obtained by a second introduction of two molecules of a diazo-compound into phenols (resorcinol), and are also called *diazo-derivatives*:—



$$\left.\begin{matrix}C_6H_5.N_2\\C_6H_5.N_2\end{matrix}\right>C_6H_2(OH)_2 = C_6H_5.N_2.C_6H_2(OH)_2.N_2.C_6H_5.$$

Dibenzene-diazo-Resorcinol. Benzene-azo-resorcinol-azo-benzene.

Analogous compounds are also obtained from the anilines, and are called *azotriple bases* (*Berichte*, **16**, 2028).

Another course, that may be pursued in obtaining the tetrazo-derivatives, employs the phenylene-diamines, $C_6H_4(NH_2)_2$, as points of departure, converting one and then the other amido- into a diazo group, and finally combining the product with phenols. Violet and blue azo-derivatives (*Berichte*, **17**, 344, 1350; **21**, Ref. 268) are produced in this manner.

The tetrazo-compounds from benzidine and tolidine are especially important (p. 652).

Azoxybenzene, $(C_6H_5)_2N_2O$, Azoxybenzide, is obtained by the reduction of nitrobenzene, or by the oxidation of amido-benzene (p. 641), the first being the preferable method.

Add 30 parts of pure nitrobenzene to a solution of 10 parts sodium in 250 parts methyl alcohol and boil for five or six hours, employing a return condenser. The unused methyl alcohol is distilled off and the residue washed with water (*Berichte*, **15**, 866, 1515). Or, 1 part of nitrobenzene is added to the boiling solution of 1 part KOH and 9 parts alcohol.

Azoxybenzene forms long, yellow needles, easily soluble in alcohol and ether, but not in water. It melts at 36°, and decomposes into azobenzene and aniline when distilled. It is converted into oxyazobenzene by digestion with sulphuric acid.

m-Dinitroazoxybenzene, $(NO_2)C_6H_4.N_2O.C_6H_4(NO_2)$, is produced when sodium methylate acts upon *m*-dinitrobenzene, $C_6H_4(NO_2)_2$. It melts at 141° (*Berichte*, **18**, 2551). *m-Diamidoazoxybenzene*, $(NH_2)C_6H_4.N_2O.C_6H_4.NH_2$, *azoxyaniline*, is obtained by the reduction of *m*-nitraniline with zinc dust and caustic soda (*Berichte*, **21**, Ref. 766). The nitration of azoxybenzene produces two *trinitroazoxybenzenes*, which form trinitro-azobenzenes by partial reduction (*Berichte*, 23, Ref. 104).

Azobenzene, $(C_6H_5)_2N_2$, Azobenzide, is formed by the action of sodium amalgam upon the alcoholic solution of nitrobenzene, and by boiling nitrobenzene with alcoholic potash.

A simpler procedure is to distil azoxybenzene with iron filings, or to reduce nitrobenzene with zinc dust and caustic potash (*Annalen*, 207, 329). Or, nitrobenzene is added to a solution of stannous chloride (calculated amount) in sodium hydroxide (p. 641).

Azobenzene forms orange-red, rhombic crystals, readily soluble in alcohol and ether, but sparingly soluble in water. It melts at 68°, and distils at 293°; its vapor density confirms the molecular formula, $C_{12}H_{10}N_2$. It is converted into benzidine by tin and hydrochloric acid. When it is heated with ammonium bisulphite and alcohol under pressure benzidine sulphaminic acid, $NH_2.C_6H_4.C_6H_4.NH.SO_3H$ (p. 650) results (*Berichte*, **18**, 1481).

The nitration of azobenzene produces *p-Nitro-azo-benzene*, $C_6H_4.N_2.C_6H_4.(NO_2)$, melting at 137°; by reduction this yields *p*-amido-azo-benzene (p. 647). The nitration of the glacial acetic acid solution yields *o-nitro-azo-benzene*, melting at 127° (*Berichte*, **18**, 2157; Ref. 441). Energetic nitration gives rise to various dinitro- and trinitro-azo-benzenes (*ibid*).

p-Dinitroazobenzene, $NO_2.C_6H_4.N_2.C_6H_4.NO_2$, melts at 206°, and is reduced by ammonium sulphide to *p*-diamido-azo-benzene (p. 648) and to diphenine (p. 650). *m-Dinitroazobenzene* is an oil; ammonium sulphide changes it to *m*-diamido-azo-benzene (*Berichte*, **18**, Ref. 627); when this decomposes *m*-phenylene diamine results.

A *dinitro-azobenzene*, melting at 117°, has been obtained by the oxidation of dinitrohydrazobenzene (*Berichte*, 21, Ref. 400; 22, Ref. 744).

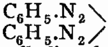
Trinitroazobenzenes, $C_{12}H_7(NO_2)_3N_2$, have been prepared by the partial reduction of the two tri-nitro-azoxybenzenes.

Nitrolic Acids, of unknown constitution, were formed in the reduction of nitrazobenzenes with ammonium sulphide in the presence of caustic potash (*Berichte*, **18**, 1136; Ref. 628).

p-Oxyazobenzene, $C_6H_5.N_2.C_6H_4(OH)$, Benzeneazophenol, is obtained on digesting diazobenzene nitrate with barium carbonate; by mixing the former with a solution of sodium phenol; by the action of para-nitrosophenol upon aniline acetate (p. 641), and by the action of concentrated sulphuric acid upon azoxyhenzene (*Berichte*, 14, 2617), as well as by heating together phenol and diazoamidobenzene. It crystallizes in orange-yellow needles, and melts at 148°.

Those oxyazo-compounds, containing a hydroxyl group in the ortho-position, with reference to the azo-group, are very probably quino-hydrazones. CS_2, on application of heat causes them to decompose, thus forming carbamido-thiophenols (*Berichte*, 22, 3233).

Dioxyazobenzenes: *p*-**Azophenol**, $C_6H_4(OH).N_2.C_6H_4(OH)$, results: by fusing para-, nitro- and nitroso-phenol with caustic potash; by the union of diazophenol nitrate with phenol, and from para-oxyazobenzene sulphonic acid (*Berichte*, 15, 3037). It consists of light brown crystals, and melts at 204°. **Benzene-azo-resorcinol**, $C_6H_5.N_2.C_6H_3(OH)_2$, is produced by adding diazobenzene nitrate or chloride to resorcinol in aqueous or alkaline solution. It forms red needles, melts at 168°, and dissolves with a yellowish-red color in alkalies. *Dibenzene-diazo-resorcinol* (γ, insoluble in alkalies) forms at the same time; it results from the decomposition of diamido-resorcinol (*Berichte*, 17, 880).

The further action of a second molecule of diazobenzene chloride upon benzene-azo-resorcinol in alkaline solution, produces two isomeric **Dibenzene-disazo-resorcinols**,  $\begin{matrix} C_6H_5.N_2 \\ C_6H_5.N_2 \end{matrix}\!\!>\!C_6H_2(OH)_2$, α and β. The α-compound is easily soluble in aqueous alkalies, forms red needles, melts at 214°, and dissolves in H_2SO_4 with a red color. The β-compound is insoluble in alkalies and dissolves in H_2SO_4 with a dark blue color (*Berichte*, 15, 2816; 17, 880).

Compounds soluble and insoluble in alkalies are almost invariably produced by the union of diazo-derivatives with phenols. In the insoluble ones the N_2-group seems almost always to occupy the ortho-position as compared with hydroxyl (*Berichte*, 16, 2862).

The **azobenzene-azo-resorcinols**, $C_6H_5.N_2.C_6H_4.N_2.C_6H_3(OH)_2$, are isomeric with the benzene-disazo-resorcinols. They form in the action of the diazo-chloride of amidoazo-benzene, $C_6H_5.N_2.C_6H_4.NH_2$, upon resorcinol (*Berichte*, 15, 2817) (compare p. 645).

p-**Amido-azo-benzene**, $C_6H_5.N_2.C_6H_4.NH_2$, is obtained in the reduction of nitro-azo-benzene with ammonium sulphide, and by the molecular transposition of isomeric diazo-amido-benzene (p. 642).

It is best prepared by the action of a mixture of potassium nitrite (1 molecule) and caustic potash upon aniline hydrochloride (2 molecules); the diazo-amido-benzene first produced in the cold is transposed by digestion into amido-azo-benzene (p. 642).

Or, freshly prepared, moist diazo-amido-benzene is dissolved in 2–3 parts aniline, $\frac{1}{10}$ part aniline hydrochloride added, and the whole digested at 40° for an hour, and then allowed to stand 24 hours, by which time the conversion into amido-azo-benzene will be fully ended (*Berichte*, 19, 1953; 21, 1633).

Aniline hydrochloride (1 molecule) can be dissolved in aniline (5–6 molecules), and mixed at 30–40° with a concentrated solution of sodium nitrite (a little less than one molecule) and digested from 1–2 hours at a temperature of 40°, when it is finally allowed to stand undisturbed for 12 hours. The addition of an excess of hydrochloric acid will cause a complete precipitation of the hydrochloride of amido-azo-benzene (*ibid*).

It crystallizes from alcohol in yellow needles or prisms, melts at 123°, and boils above 360°. It forms crystalline salts with one equivalent of acid; these are yellow and violet colored, and impart an intense yellow to silk and wool. The HCl-salt crystallizes from hydrochloric acid in blue needles or scales. MnO_2 and sulphuric acid oxidize it to quinone. It is decomposed into para-diamido-benzene and aniline by tin and hydrochloric acid, digestion with ammonium sulphide, or boiling with hydrochloric acid (p. 645).

Commercial *Aniline Yellow* consists usually of amido-azo-benzene oxalate. The so-called *Acid Yellow* or *Pure Yellow* is a mixture of amido-azo-benzene sulphonic acids, and is prepared by the action of sulphuric acid on the amido azo-compound, or by converting sulphanilic acid, $C_6H_4(SO_3.H).NH_2$, into the diazo-compound, and then treating with aniline (*Berichte*, 22, 850).

Phenyl-*p*-amido-azo-benzene, $C_6H_5.N_2.C_6H_4.NH.C_6H_5$, is isomeric with induline. It is produced from diazobenzene chloride and diphenylamine. It consists of golden-yellow leaflets, melting at 82°. Its sulphonic acid is tropæoline OO (p. 651).

Indulines are obtained on heating *p*-amido-azo-benzene or other *p*-amido-azo-derivatives with aniline hydrochlorides, whereas the *o*-amido-azo-compounds yield the *eurhodines* (*Berichte*, 19, 441).

Nitrous acid converts HCl-amido-azobenzene into the *diazo-chloride*, $C_6H_5.N_2.C_6H_4.N_2Cl$; the diazo-group in this can be replaced by copper sulphate and potassium cyanide. The resulting **azo-benzene cyanide**, $C_6H_5.N_2.C_6H_4.CN$, melts at 10° and is changed to azobenzene carboxylic acid, $C_6H_5.N_2.C_6H_4.CO_2H$ (*Berichte*, 19, 3023), by boiling alkalies.

The **disazo- or tetrazo-anilines, or phenols**, result from the action of azo-benzene diazo-chloride, $C_6H_5.N_2.C_6H_5.N_2Cl$, upon anilines and phenols. **Disazo-benzene**, $C_6H_5.N_2.C_6H_4.N_2.C_6H_5$, the basis of these derivatives, has been obtained from its amido-compound. It is very similar to azo-benzene, and melts at 98° (*Berichte*, 21, 2145).

Diamido-azo-benzene, $C_{12}H_{12}N_4 = C_6H_5.N_2.C_6H_3(NH_2)_2$, Benzene-azo-phenylene-diamine, is produced by the action of diazo-benzene-nitrate upon meta-phenylene-diamine (p. 643), and consists of yellow needles, melting at 117°. Its hydrochloric acid salt occurs in trade under the name *chrysoïdine*, and dyes orange-red. Reduction changes it to aniline and unsymmetrical triamido-benzene, $C_6H_3(NH_2)_3$.

Symmetrical ***p*-Diamido-azo-benzene**, $H_2N.C_6H_4.N_2.C_6H_4.NH_2$, has been prepared by reducing nitroacetanilide, $NO_2.C_6H_4.NH.C_2H_3O$, with zinc dust and alkali; also, from diazo-phenylene diamine, etc. (*Berichte*, 18, 1145), and by the reduction of *p*-dinitroazobenzene (see above) (*Berichte*, 18, Ref. 628). It crystallizes from alcohol in yellow needles, melting at 235°.

Its tetra-alkylic derivatives are the so-called *Azylines*. They are formed when nitric oxide acts upon the tertiary anilines (dialkylanilines) (*Berichte*, 16, 2768):—

$$2C_6H_5.NR_2 \quad \text{yield} \quad R_2N.C_6H_4.N_2.C_6H_4.R_2N,$$

and in the action of the diazo-compounds of dimethyl-*p*-phenylene diamine (p. 625) upon tertiary anilines (*Berichte*, 18, 1143):—

$$(CH_3)_2N.C_6H_4.N_2Cl + C_6H_5N(CH_3)_2 = (CH_3)_2N.C_6H_4.N_2.C_6H_4N(CH_3)_2 + HCl.$$

The azylines are red, basic dyes, which dissolve in hydrochloric acid with a purple-red and in acetic acid with an emerald-green color. By reduction (stannous chloride, tin and hydrochloric acid) they yield two molecules of dialkylic *p*-phenylene-diamine. They are decomposed when heated to 100° with alkyl iodides (4 molecules); the products in this case are tetra-alkylic para-phenylene-diamines.

Triamido-azo-benzene, $C_{12}H_{13}N_5 = H_2N.C_6H_4.N_2.C_6H_3\left<\begin{matrix}NH_2\\NH_2\end{matrix}\right.$, is formed when nitrous acid acts upon metaphenylene-diamine, $C_6H_4(NH_2)_2$. At first, by transformation of an amido-group, we obtain a diazo-compound, which further reacts on a second molecule of the diamine. It forms salts with one, two and three equivalents of the acids; of these the diacid are the most stable, while water decomposes the triacid. Its hydrochloric acid salt is commercial *Phenylene Brown* (Manchester-brown, Bismarck-brown), which is applied in dyeing cotton and coloring leather.

Azotoluenes, $CH_3.C_6H_4.N_2.C_6H_4.CH_3$.

These are obtained, like azobenzene, from the three nitrotoluenes by the action of sodium amalgam or zinc dust in alkaline solution. *Ortho-* and *meta-*azotoluene form red crystals; the first melting at 137° and the latter at 55°. *Para-*azotoluene crystallizes in golden yellow needles, melting at 143°.

The action of sodium methylate upon para-nitrotoluene produces diamidostilbene, $C_6H_4(NH_2).CH:CH.C_6H_4(NH_2)$ (*Berichte*, 19, 3237).

Of the three diazoamidotoluenes, $C_6H_4.CH_3.N_2.NH.C_6H_4(CH_3)$, the ortho- and meta- rearrange themselves into the corresponding amidoazotoluenes while the para-derivative remains unaltered (see p. 642). The azo-group takes up the para position with reference to the amido-group:—

$CH_3.C_6H_4.NH_2$ *o*-Toluidine.	yields	$\underset{(2,\ 1.)}{CH_3.C_6H_4}.N_2.\underset{(1,\ 3,\ 4.)}{C_6H_3.(CH_3)NH_2}$.
$CH_3.C_6H_4.NH_2$ *m*-Toluidine.	yields	$\underset{(3,\ 1.)}{CH_3.C_6H_4}.N_2.\underset{(1,\ 2,\ 4.)}{C_6H_3.(CH_3).NH_2}$.

Amidoazotoluene, from *o*-toluidine, forms yellow leaflets. It melts at 100°. *Amidoazotoluene,* from *m*-toluidine, melts at 80°. In paratoluidine the para-position is occupied; the azo-group therefore takes up the *ortho*-position with reference to the amido group. The resulting *ortho-amidoazotoluene,* with the amido- and azo-groups, in the ortho-position, melts at 118°.

Ortho-amidoazo-derivatives like these exhibit a varying deportment. Chromic acid oxidizes them to pseudoazo-imido compounds, and when heated with aniline they yield *eurhodines.*

See *Berichte*, 23, 1738 for azoxytoluenes.

Hydrazo-benzene, $C_{12}H_{12}N_2 = C_6H_5.NH.NH.C_6H_5$ (p. 640), is obtained by the action of H_2S and ammonia upon the alcoholic solution of azo-benzene, or by boiling the latter with zinc dust and alcohol. It is readily soluble in alcohol and ether, crystallizes in colorless plates, has an odor resembling that of camphor, melts at 131°, and further decomposes into azo-benzene and aniline. When its alcoholic solution is exposed to the air it oxidizes to azo-benzene. Hydrazobenzene (like phenylhydrazine) unites with aldehydes on heating, to form compounds known as hydrazoïnes.

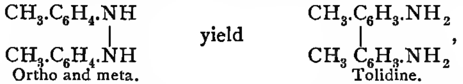
The benzaldehyde derivative, *Benzhydrazoïne*, $C_6H_5.CH\left\langle\begin{matrix}N.C_6H_5\\N.C_6H_5\end{matrix}\right.$, melts at 55° (*Berichte*, 19, 2239). It also unites with acetoacetic ester and acetone-dicarboxylic esters, forming pyrazole derivatives.

It does not form salts with acids, but concentrated mineral acids occasion in it an interesting transposition, resulting in the appearance of the isomeric, basic *benzidine* (diamido-diphenyl):—

$$C_6H_5.NH.NH.C_6H_5 \quad \text{forms} \quad NH_2.C_6H_4.C_6H_4.NH_2.$$

Derivatives of benzidine are produced when it is heated with organic acids (*Berichte*, 17, 1181). In benzidine the union of the benzene groups occurs in the two para-positions. With benzidine (especially in the warm) there is also produced isomeric *o*-*p*-diamido-diphenyl, $\begin{matrix}C_6H_4.NH_2(1, 4)\\ \\ C_6H_4.NH_2(1, 2)\end{matrix}$

Other hydrazo-compounds are similarly converted into diphenyl derivatives, but usually these are only such that have the para-positions, with reference to the imide groups, free. Thus, *o*- and *m*-hydrazotoluene yield the corresponding tolidines (diamidoditolyl derivatives):—



$$\begin{matrix}CH_3.C_6H_4.NH\\ |\\ CH_3.C_6H_4.NH\end{matrix} \quad \text{yield} \quad \begin{matrix}CH_3.C_6H_3.NH_2\\ |\\ CH_3\ C_6H_3.NH_2\end{matrix},$$

Ortho and meta. Tolidine.

while *p* hydrazotoluene is decomposed by strong acids. The para-azo-compounds, however, can also be directly changed to diphenyl derivatives by the action of stannous chloride and sulphuric acid (*Berichte*, 17, 463; 19, 2970).

Dinitrohydrazo-benzenes, $C_6H_3(NO_2)_2.NH.NH.C_6H_5$. Two isomerides have been obtained by acting upon dinitrochlorbenzene with phenylhydrazine (*Berichte*, 21, Ref. 571).

p-Diamidohydrazobenzene, $C_6H_4(NH_2).NH.NH.C_6H_4(NH_2) = C_{12}H_{14}N_4$, formerly called *diphenine*, results from the action of ammonium sulphide upon para-dinitro-azo-benzene (*Berichte*, 18, 1136). It consists of yellow crystals, melts at 145°, and yields red colored salts with acids. Heated with ammonium sulphide it breaks up into 2 molecules of meta-diphenylene-diamine. *Hydrazobenzene-disulphonic Acid*, $C_{12}H_{10}.N_2.(SO_3H)_2$, has been obtained by the reduction of *m*-nitrobenzene sulphonic acid. Hydrochloric acid converts it into benzidine disulphonic acid (*Berichte*, 21, Ref. 323; 23, 1053).

Hydrazotoluenes, $CH_3.C_6H_4.NH.NH.C_6H_4.CH_3$.

The three derivatives of this class are prepared from three azotoluenes (p. 649) by the action of sodium amalgam, or by heating with ammonium sulphide. The *ortho*-compound melts at 165°; the *meta* is liquid, and the *para* consists of large plates, melting at 124°.

Ortho- and meta-hydrazotoluene are readily changed by mineral acids into the isomeric tolidines, $NH_2.C_7H_6.C_7H_6.NH_2$.

Azo-dyes.

Below are mentioned some of the innumerable, complicated azo-compounds, which are applied technically as *dyes*. They are either azo-amido-derivatives (*azo-bases*) which form salts with acids, or azo-phenol-compounds (*azo-acids*) (p. 644), yielding salts with bases. These salts represent the commercial dyes. In many cases the sulphonic acids of the azo-bases and azo-acids (the *tropæolines*, p. 644) are better adapted for the purpose, as their alkali salts are very stable, and usually afford dyes which dissolve readily in water.

The azo-dyes are made soluble by forming their alkaline bisulphite derivatives, which are soluble in water. These are prepared by heating the azo-compounds with sodium or potassium bisulphite in aqueous or alcoholic solution. On heating these combinations with steam or dilute alkalies they split up into their compounds and upon this behavior is based their application as colors for mordanted materials (*Berichte*, 18, 1479).

Arbitrary names are assigned these *dyes*, with the addition of the letters Y (yellow), O (orange), and R (red), whose number approximately expresses the intensity of the color. They color wool and silk directly, cotton after it has been mordanted. Recently violet and blue azo-dyes have been successfully prepared (mainly tetra-azo-compounds, p. 645).

Tropæoline, O or R (Chrysoïne, resorcin-yellow), $C_6H_4(SO_3H).N_2.C_6H_3(OH)_2$, Resorcin-azo-benzene sulphonic acid, is obtained from para-diazo-benzene sulphonic acid and resorcinol (*Berichte*, 11, 2195).

Tropæoline, OO (Orange IV), $C_6H_4(SO_3H).N_2.C_6H_4.NH.C_6H_5$, Diphenyl-amine-azo-benzene sulphonic acid, is obtained from diazobenzene sulphonic acid and diphenylamine in alcoholic solution. It is used as an indicator in alkalimetry (*Berichte*, 16, 1989). By decomposition it yields sulphanilic acid, $C_6H_4(NH_2).SO_3H$, and amido-diphenylamine (p. 603).

Helianthine, Methyl Orange (Orange III), $C_6H_4(SO_3H).N_2.C_6H_4.N(CH_3)_2$, Dimethylaniline-azo-benzene-sulphonic acid, is formed from diazobenzene sulphonic acid and dimethyl aniline (*Berichte* 10, 528). Consult *Berichte*, 17, 1490, for another method of preparation. This and the analogous **ethyl orange** (from diethyl aniline) serve as delicate indicators in alkalimetry; mineral acids convert the alkaline orange-colored solution into a rose-red. CO_2, H_2S and acetic acid do not act on it in the cold (*Chem. Zeit.*, VI, 1249; *Berichte*, 18, 3290). In decomposition *helianthine* yields sulphanilic acid and para-amido-dimethyl aniline (p. 601). *Monomethyl-* and *Mono-ethyl Orange*, $C_6H_4(SO_3H).N_2.C_6H_4.NH(C_2H_5)$, are similarly prepared by the action of diazo-benzene-sulphonic acid upon methyl- and ethyl-aniline. By its decomposition methyl- and ethyl-*p*-phenylene diamine, $H_2N.C_6H_4.NH.CH_3$ (*Berichte*, 20, 924), are produced.

The azo-dyes obtained from the naphthalene derivatives, are of great value.

Tropæoline OOO, No. I (Orange I), is formed from diazobenzene sulphonic acid and α-naphthol. If β-naphthol, in alkaline solution, be used, then the product will be *β-naphthol-azo-benzene sulphonic acid*, $C_{10}H_6(OH).N_2.C_6H_4.SO_3H$. Its sodium salt is the *β-naphthol orange* (Orange II) of trade.

Various **Ponceaus** and **Bordeaus** (R, RR, G, GG, etc.) are obtained by means of β-naphthol disulphonic acids from diazo-xylidines and diazo-cumidines (p. 624). **Biebrich Scarlets** are obtained from the sulphonic acids of amido-azo-benzene, $C_6H_5.N_2.C_6H_4.NH_2$ (the chlorides) with β-naphthol. They are tetrazo-compounds (*Berichte*, 13, 1838). **Croceïn Scarlet** (*Berichte*, 15, 1352), from β-naphthol sulphonic acid, is also of importance.

Fast Brown is a disazo- or tetrazo-compound. It is the disulphonic acid ot α-naphthol disazobenzene, which may be prepared by the union of two molecules of diazo-sulphanilic acid with α-naphthol (*Berichte*, 21, 3241).

Diazo-naphthalene sulphonic acid and β-naphthol combine and produce *β-Naphtholazonaphthalene sulphonic acid*, $C_{10}H_6(OH).N_2.C_{10}H_6.SO_3H$. The sodium salt of the latter is *fast red* or *rocellin*, which serves as a substitute for archil or cochineal.

The tetrazo-dyes, derived from *benzidine* and *tolidine*, are especially important, as they color unmordanted cotton, and the product is not affected by soap. *Congo red*, *chrysamine*, *azo-blue*, *benz-azurine*, *Congo yellow*, etc., are of this class (see Benzidine).

Mixed Azo compounds.

In this class the azo-group is linked to a benzene nucleus, and to a paraffin residue.

Azo-phenyl-methyl, $C_6H_5.N_2.CH_3$, Benzene azomethane, is made by oxidizing α-methylphenyl hydrazine (p. 657) with mercuric oxide. It is a yellow, volatile oil, with a peculiar odor. It boils at 150°. Sodium amalgam reduces it to α-methylphenyl hydrazine (*Berichte*, 18, 1742). **Azo-phenyl-ethyl**, $C_6H_5.N_2.C_2H_5$, has been similarly prepared from α-ethyl-phenyl-hydrazine. It closely resembles the methyl compound. It melts about 180°.

Azo-phenyl-nitroethyl, $C_6H_5.N_2.CH(NO_2).CH_3$, **Benzene-azo-nitroethane**, is obtained by the action of diazobenzene nitrate, $C_6H_5.N_2.NO_3$, upon sodium nitroethane. It crystallizes in orange colored laminæ, melting at 137°. It behaves like an acid, dissolving in alkalies with a blood-red color, and forming basic salts, containing two equivalents of the bases (*Berichte*, 8, 1076; 9, 384).

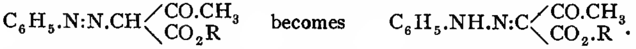
Compounds, regarded as *mixed azo-derivatives*, have been similarly prepared by the interaction of benzene-diazo-salts and various fatty bodies. However, a transposition occurs when they are produced and *hydrazones* result (p. 656) (see Japp, *Annalen*, 247, 190; *Berichte*, 21, Ref. 725; V. Meyer, *Berichte*, 21, 11).

Thus, when benzene diazo-salts act upon malonic ester, the product is not the expected *benzene-azo-malonic acid*, but its isomeride, *phenyl hydrazon-mesoxalic acid*:—

$C_6H_5.N_2.CH(CO_2H)_2$	becomes	$C_6H_5.NH.N{:}C(CO_2H)_2$,
Benzene-azo-malonic Acid.		Phenyl-hydrazon-mesoxalic Acid.

as it is also formed by the action of phenyl-hydrazine upon mesoxalic acid (p. 434).

Similarly, diazo-benzene chloride and aceto-acetic ester do not produce *benzene-azo-acetic ester*, but the hydrazone of aceto-glyoxylic ester (*Berichte*, 20, 2121):



$$C_6H_5.N{:}N.CH\left\langle\begin{matrix}CO.CH_3\\CO_2R\end{matrix}\right. \quad \text{becomes} \quad C_6H_5.NH.N{:}C\left\langle\begin{matrix}CO.CH_3\\CO_2.R\end{matrix}\right. .$$

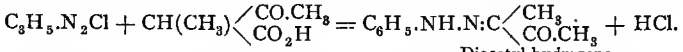
Benzene-diazo chloride acts upon benzoyl-acetic ester in the same manner. Benzene-azo-acetone, $C_6H_5.N_2.CH_2.CO.CH_3$ (*Berichte*, 17, 2415), resulting from the decomposition of the ester that is formed, is the hydrazone of pyro-racemic aldehyde, $C_6H_5.NH.N{:}CH.CO.CH_3$ (p. 323).

Benzene diazo-salts displace the acetyl group of mono-alkylic aceto-acetic esters. In doing this, they do not form the *benzene-azo-fatty acids*, but the *hydrazones* of α-ketonic acids (*Berichte*, 20, 3398):—

$$C_6H_5.N_2.CH\left\langle\begin{matrix}CH_3\\CO_2R\end{matrix}\right. \quad \text{becomes} \quad C_6H_5.NH.N{:}C\left\langle\begin{matrix}CH_3\\CO_2R\end{matrix}\right. .$$

Benzene-azo-propionic Acid. Hydrazon-pyro-racemic Acid.

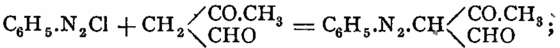
When the benzene-diazo-salts act upon the free alkyl-aceto-acetic esters, carbon dioxide is evolved, and hydrazones of *o*-diketones result (*Berichte*, 21, 549):—



$$C_8H_5.N_2Cl + CH(CH_3)\Big\langle{CO.CH_3 \atop CO_2H} = C_6H_5.NH.N{:}C\Big\langle{CH_3 \atop CO.CH_3} + HCl.$$

Diacetyl-hydrazone.

However, in other cases, the action of the benzene-diazo-salts proceeds in the normal way. Rearrangements do not occur, and *mixed azo*-compounds *are* produced (*Berichte*, 21, 1697). Acetaldehyde reacts in this manner (p. 323):—



$$C_6H_5.N_2Cl + CH_2\Big\langle{CO.CH_3 \atop CHO} = C_6H_5.N_2.CH\Big\langle{CO.CH_3 \atop CHO};$$

Benzene-azo-acetaldehyde.

also, aceto-acetone, $CH_3.CO.CH_2.CO.CH_3$, and dibenzoyl-methane. The mixed azo-compounds, obtained from them, dissolve unaltered in alkalies, and being β-carbonyl derivatives, unite with phenyl-hydrazine and form hydrazones, which lose water and become pyrazole-derivatives (p. 327). Benzene-azo-cyanacetic ester, $C_6H_5.N_2.CH(CN).CO_2R$, is thus formed from cyanacetic ester and benzene-diazo-chloride (*Berichte*, 21, Ref. 354).

HYDRAZINE COMPOUNDS.

The hydrazines studied by E. Fischer in 1877 (*Annalen*, 190, 67) are intimately related to the diazo-compounds:—

$C_6H_5.N{:}N.O.NO_2$.	$C_6H_5.NH.NH_2.HNO_3$.
Diazobenzene-nitrate.	Hydrazine Nitrate.

They are derivatives of diamide or hydrazine, $H_2N.NH_2$, which has only recently been obtained in a free condition (*Berichte*, 20, 1632). (p. 166). They are formed:—

1. By the action of alkaline sulphites upon the diazo-derivatives. On allowing neutral potassium sulphite to act in the cold upon diazobenzene nitrate or hydrochloride, the yellow colored potassium salt of diazobenzene-sulphonic acid will be produced at first (p. 636):—

$$C_6H_5.N_2.NO_3 + SO_3K_2 = C_6H_5.N_2.SO_3K + NO_3K;$$

but should the primary potassium sulphite act at 20–30°, the diazo-sulphonic acid will be further reduced, and colorless potassium benzene hydrazine-sulphonate will be formed immediately:—

$$C_6H_5.N_2.SO_3K + H_2 = C_6H_5.N_2.H_2.SO_3K.$$

The yellow diazosulphonate can be reduced to the hydrazine compound by sulphurous acid, or better, with zinc dust and acetic acid.

When the sulphonate is heated with hydrochloric acid hydrazine hydrochloride is produced:—

$$C_8H_5.N_2.H_2.SO_3K + HCl + H_2O = C_6H_5.N_2H_3.HCl + SO_4KH;$$

the alkalies separate the free hydrazine, $C_6H_5.N_2H_3$.

Preparation.—In making phenyl hydrazine (benzene hydrazine) dissolve 20 parts of aniline in 50 parts of hydrochloric acid (sp. gr. 1.19) and 80 parts water, and then add the equivalent amount of sodium or potassium nitrite (dissolved in 2 parts water). The solution contains diazobenzene chloride, $C_6H_5.N_2Cl$, and is gradually added to a cold solution of sodium sulphite (2 molecules); sodium phenyl hydrazine sulphonate then separates, but is mixed with the yellow diazo-sulphonate, which is completely reduced by digestion with zinc dust (with addition of acetic acid). The filtered, colorless solution of the hydrazine-sulphonate is boiled with concentrated hydrochloric acid (⅓ volume), and the hydrazine separated by means of caustic soda (*Annalen*, 190, 78). A modified method for the preparation of phenylhydrazine will be found in the *Berichte*, 20, 2463.

The *sulphazides*, *e. g.*, $C_6H_5.NH.NH.SO_2.C_6H_5$, *phenyl-benzene sulphazide*, are prepared by the action of free sulphurous acid upon the acid solution of diazobenzene salts, or by the interaction of nitrous acid, and an alcoholic aniline base supersaturated with SO_2 (*Berichte*, 20, 1238). These are to be regarded as benzene sulphinic acid derivatives (p. 662) of the hydrazines. They are also formed when benzene sulphonic acid chloride, $C_6H_5.SO_2Cl$, and benzene sulphinic acid, $C_6H_5.SO_2H$, act upon phenyl hydrazine (*Berichte*, 18, 893). Warm alkalies resolve the sulphazides into benzene and benzene-sulphinic acid: $C_6H_5.NH.NH.SO_2.C_6H_5$ yields $C_6H_6 + N_2 + C_6H_5.SO_2H$. Mercuric oxide oxidizes phenyl-benzene-sulphazide to benzene-sulphin-diazobenzene, $C_6H_5.N_2.SO_2.C_6H_5$, and conversely can be obtained from the latter (from diazobenzene nitrate and sodium benzene sulphinide) by reduction with zinc dust.

2. By the action of stannous chloride and hydrochloric acid upon the diazo-chlorides (V. Meyer, *Berichte*, 16, 2976):—

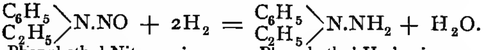
$$C_6H_5.N_2Cl + 2SnCl_2 + 4HCl = C_6H_5.N_2H_3.HCl + 2SnCl_4.$$

This procedure affords results which are especially good, if the hydrazine chloride (*e. g.*, naphthyl hydrazines) dissolves with difficulty (*Berichte*, 17, 572).

3. By the reduction of diazo-amido-compounds in alcoholic solution with zinc dust and acetic acid, when they decompose into anilines and hydrazines:—

$$\underset{\text{Diazo-amido-benzene.}}{C_6H_5.N_2.NH.C_6H_5} + 2H_2 = \underset{\text{Phenyl-hydrazine.}}{C_6H_5.N_2H_3} + \underset{\text{Aniline.}}{NH_2.C_6H_5.}$$

4. By the reduction of the nitroso-amines (pp. 164 and 598) with zinc dust and acetic acid:—



$$\underset{\text{Phenyl-ethyl Nitrosamine.}}{\left.\begin{matrix}C_6H_5\\C_2H_5\end{matrix}\right\rangle N.NO} + 2H_2 = \underset{\text{Phenyl-ethyl Hydrazine.}}{\left.\begin{matrix}C_6H_5\\C_2H_5\end{matrix}\right\rangle N.NH_2} + H_2O.$$

The benzene hydrazines are very similar to those of the marsh-gas series, but are less basic and in consequence are only capable of uniting with one equivalent of acids to form salts. Generally they are easily fusible and boil with but slight decomposition.

When boiled with copper sulphate or ferric chloride (*Berichte*, 18, 786) the phenylhydrazines throw off nitrogen and become benzenes—this reaction will also serve for the replacement of the diazo-group by hydrogen (p. 633). The liberated nitrogen also answers for the quantitative estimation of the hydrazines (*Berichte*, **18**, 3177).

The hydrogen of the imide group in the phenylhydrazines can be replaced by sodium, the nitroso groups by alkyls and acid radicals; alkyl- and acid derivatives of the NH_2-group (see below) are also known.

Phenylhydrazones (p. 656) are produced by the union of the phenylhydrazines with aldehydes, ketones, aldehydic and ketonic acids.

Although the hydrazines are very stable in the presence of reducing agents, they are readily oxidized and destroyed. They, therefore, reduce salts of the heavy metals and precipitate cuprous oxide from *Fehling's* solution; in this case the primary hydrazines and the *a*-alkyl derivatives react even in the cold.

The phenyl hydrazines may be readily reconverted into diazo-compounds by moderated oxidation; this is effected by the action of mercuric oxide upon their sulphonates:—

$$C_6H_5.NH.NH_2.HX + 2O = C_6H_5.N{:}N.X + 2H_2O.$$

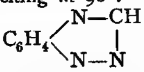
Phenylhydrazine, $C_6H_5.NH.NH_2$, is obtained from benzene diazochloride by reduction with sodium sulphite or stannous chloride (p. 653). It is a colorless, peculiar-smelling oil, solidifying, when cooled, to plate-like crystals, melting at 23°; sp. gr. 1.091 at 21°. It boils at 241–242° with slight decomposition (*Annalen*, **236**, 198). It dissolves with great difficulty in cold water, but readily in alcohol and ether. It assumes a light brown color on exposure to the air. It serves as an important reagent for the detection of aldehydes and ketones (see above) and has been applied in a very great number of syntheses (that of antipyrine).

Nitrous acid converts it into diazobenzene imide. When sodium nitrite acts upon HCl-phenylhydrazine in the cold *nitroso-phenylhydrazine*, $C_6H_5.N(NO).NH_2$, separates as a yellow-brown oil, solidifying to yellow laminæ. Dilute alkalies decompose this compound into water and diazo-benzene-imide.

Metallic sodium dissolves in phenylhydrazine, forming the sodium derivative, $C_6H_5.NNa.NH_2$. This is a yellowish red, amorphous mass.

Alkyls and acid residues can replace the sodium, thus producing β-phenylhydrazine derivatives (p. 657) (*Berichte*, **19**, 2448; **22**, Ref. 604).

Substituted derivatives may be obtained from the substituted anilines (*Berichte*, **22**, 14). *p*-**Bromphenylhydrazine,** $C_6H_4Br.N_2H_3$, melts at 106° and forms hydrazines. *o*-**Nitrophenylhydrazine,** $C_6H_4(NO_2).N_2H_3(1, 2)$, from *o*-nitraniline, forms brilliant red needles, melting at 90°. Sodium amalgam reduces its formyl compound to *Benzotriazine*,



$$C_6H_4\begin{matrix}\diagup N{-}CH \\ \qquad | \\ \diagdown N{-}N\end{matrix}$$

(*Berichte*, **22**, 2806).

The sulphonates are formed by the reduction of diazobenzene-sulphonic acids with sodium sulphite or stannous chloride (*Berichte*, **22**, Ref. 216), and also by the direct action of concentrated sulphuric acid upon the phenylhydrazines (*Berichte*, 18, 3172).

p-**Hydrazine-benzenesulphonic Acid**, $C_6H_4.(NH.NH_2)SO_3H$, is not readily soluble in water. It is used in the preparation of tartrazine (p. 492).

The digestion of phenylhydrazine with $K_2S_2O_7$, or the addition of diazobenzene nitrate to a solution of potassium bisulphite, gives rise to the potassium salt of **Benzene-hydrazine Sulphonic Acid**, $C_6H_4NH.NH.SO_3H$. The salt crystallizes in scales, dissolving in water with difficulty.

Phenylhydrazones (*Berichte*, 21, 984).

Phenylhydrazones, or hydrazones, are produced by the action of phenylhydrazine upon carbonyl compounds, when the amido-group reacts with the CO-group:—

$$C_6H_5.NH.NH_2 + CHO.CH_3 = \underset{\text{Aldehyde Hydrazone.}}{C_6H_5.NH.N{:}CH.CH_3} + H_2O.$$

This is confirmed by the analogous deportment of the β-alkyl phenylhydrazines (p. 657):—

$$C_6H_5.N(CH_3).NH_2 + CO(CH_3)_2 = \underset{\text{Acetone-methyl-phenyl Hydrazone.}}{C_6H_5.N(CH_3).N{:}C(CH_3)_2} + H_2O;$$

as well as by the formation of indol derivatives from the hydrazones, and by the behavior of benzal-phenyl hydrazone (*Berichte*, 20, 2487).

The reaction proceeds in an aqueous or alcoholic solution (*Berichte*, 17, 573).

A solution of 1 part HCl-phenylhydrazine with 1½ parts sodium acetate in 8–10 parts water, is well adapted as a reagent for the compounds soluble in water.

The aldoximes and acetoximes, or isonitroso-compounds, react in a similar manner. The phenyl-hydrazine replaces the isonitroso group (*Berichte*, 19, 1205):—

$$C_6H_5.NH.NH_2 + HO.N{:}C(CH_3)_2 = C_6H_5.NH.N{:}C(CH_3)_2 + NH_2.OH.$$

A peculiar formation of hydrazones is that in which benzene diazo-salts act upon different CH- and CH_2-compounds (p. 652). The α-diketone derivatives yield *mono-* and *di-hydrazones*; the latter are called *osazones* (p. 326). The glucoses (aldehyde- and ketone-alcohols) deport themselves similarly, as they yield both hydrazones and osazones (p. 501). The β-keto-compounds first form hydrazones with one molecule of phenylhydrazine, but by the exit of water, they condense to *pyrazole-* and *pyrazolon*-derivatives (p. 339).

The hydrazones are usually crystalline compounds, insoluble in water. They are yellow or brown in color. They almost invariably decompose upon fusion, hence their melting points are only correct when they are heated rapidly. If digested with mineral acids they absorb water, more or less readily, and revert to their components. Pyroracemic acid brings about the decomposition more easily (*Berichte*, 22, Ref. 674).

Some hydrazones are decomposed by reduction (sodium amalgam, tin and hydrochloric acid, or sodium and absolute alcohol), when they yield anilines and amido acids (see amido-valeric acid, p. 372) (*Berichte*, 20, 3399).

Nearly all phenyl hydrazones are condensed, upon heating them with concentrated mineral acids, or zinc chloride, to *indol* derivatives. Ammonia is expelled.

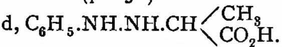
The hydrazones have, in most cases, been mentioned in connection with the corresponding carbonyl compounds. Those of the aldehydes and ketones of the fat series are generally yellow oils (*Annalen*, 236, 126, 137).

Ethidene Phenyl-hydrazone, $CH_3CH{:}N_2H.C_6H_5$ (isomeric with benzene-azo-ethane), becomes crystalline in the cold. It boils at 250°. **Propidene Hydrazone,** $C_2H_5.CH{:}N_2H.C_6H_5$, boils undecomposed under diminished pressure.

Acetone Hydrazone, $(CH_3)_2.C{:}N_2H.C_6H_6$, can also be distilled under diminished pressure.

Pyroracemaldehydrazone, $C_6H_5.NH.N{:}CH.CO.CH_3$ (p. 323), formerly considered as **Benzene-azo-acetone,** $C_6H_5.N_2.CH_2.CO.CH_3$ (p. 652), is produced by the ketone decomposition of hydrazone-acetoglyoxylic ester, induced upon digesting it with alkalies (*Berichte*, 17, 2415). It crystallizes in yellowish-brown prisms, melting at 149°. Sodium ethylate and alkyl iodides, or chloracetic ester, displace the hydrogen of its imide group (*Berichte*, 29, 3398). Phenyl hydrazine converts it into the *osazone* of pyroracemic aldehyde, $CH_3.C(N_2H.C_6H_5).CH(N_2H.C_6H_5)$ (p. 323), which can also be obtained from acetol and isonitroso-acetone (*Berichte*, 20, 3399). It does not react with phenyl cyanate (*Berichte*, 23, 496).

Pyroracemic-acid Hydrazone, $CH_3.C(N_2H.C_6H_5).CO_2H$ (p. 332), is identical with *benzene-azo-propionic acid* (p. 652). Sodium amalgam converts it into

Hydrazido-propionic Acid,

$C_6H_5.NH.NH.CH\begin{cases}CH_3\\CO_2H.\end{cases}$

Glyoxylic-acid Hydrazone, $C_6H_5.NH.N{:}CH.CO_2H$, by reduction yields **Phenylhydrazido-acetic Acid,** $C_6H_6.NH.NH_2.CH_2.CO_2H$, which can also be prepared by reducing nitroso-phenylglycin, $C_6H_5.N(NO).CH_2.CO_2H$.

Alkylized Hydrazines:—

$C_6H_5.NH.NH.CH_3$	and	$C_6H_5.N(CH_3).NH_2$.
α-Methyl-phenyl-hydrazine.		β-Methyl-phenyl-hydrazine.

The α-derivatives are termed *symmetrical*, the β-compounds *unsymmetrical* alkylphenylhydrazines. Both isomerides are produced by the action of alkyl bromides upon phenylhydrazine (*Annalen*, 199, 325; *Berichte*, 17, 2844). The β-class are also obtained by the action of ethyl bromide upon sodium phenylhydrazine (*Berichte*, 19, 2420, 22, Ref. 664), and by the reduction of the nitrosamines (p. 654). The α-derivatives reduce Fehling's solution even at the ordinary temperature (like the primary hydrazines), but the β-class only act in this way after warming. By oxidation (chiefly by means of mercuric oxide) the α-derivatives pass into azo-compounds, like azophenylmethyl, $C_6H_5.N.N.CH_3$ (p. 652), which by reduction revert to the original bodies. The β-derivatives, on the contrary, liberate it, and become secondary anilines, or they form the *tetrazones* (see below). Nitrous acid causes the β-compounds to split off the NH_2 group and yield nitrosamines, *e.g.*, $C_6H_5.N(NO).CH_3$.

α-Methylhydrazine, $C_6H_5.NH.NH(CH)_3$, results upon distilling methyl dibenzoylphenyl hydrazine (p. 658) with potash. It is rather unstable. It is easily oxidized by mercuric oxide to azophenylethyl (*Berichte*, 18, 741).

α-Ethyl-phenyl hydrazine, $C_6H_5.NH.NH(C_2H_5)$, is produced when azophenyl-ethyl is reduced with sodium amalgam (*Annalen*, 199, 330). It is a colorless oil. Mercuric oxide or nitrous acid will reoxidize it to azophenyl-methyl.

β-Methyl-phenyl hydrazine, $C_6H_5N(CH_3).NH_2$, and *β-Ethyl-phenyl hydrazine* are obtained by the reduction of nitroso-methyl and nitroso-ethyl aniline by means of zinc dust (p. 654); the first boils about 227° (*Annalen*, 236, 198), the second at 232° (*Berichte*, 19, 2450). The ethyl compound unites with ethyl iodide to the bromide, $C_6H_5.N(C_2H_5)_2Br.NH_2$, which by reduction yields diethyl-aniline (*Berichte*, 17, 2844).

α-Allyl-phenyl hydrazine, $C_6H_5.NH.NH.C_3H_5$, boils at 177° under 110 mm. pressure (*Berichte*, 22, 2233).

β-Ethylene-phenyl hydrazine, $C_2H_4(N(NH_2).C_6H_5)_2$, from sodium phenyl hydrazine and ethylene bromide, melts at 90° (*Berichte*, 22, Ref. 810).

a-Diphenyl-hydrazine, $(C_6H_5)_2.N.NH_2$, isomeric with benzene hydrazine from nitrosodiphenyl-amine, crystallizes in plates, melting at 34°, and boiling at 220° under 50 mm. pressure, or dissolves in sulphuric acid with a dark blue color. (*Berichte*, 22, Ref. 582). It forms rather insoluble diphenyl-hydrazones when digested with the glucoses (p. 501).

Tetrazones.

These are produced from the β-alkyl-phenylhydrazines by oxidation with mercuric oxide in alcoholic or ethereal solution, or by means of a dilute ferric chloride solution :—

$$2C_6H_5.N(CH_3).NH_2 + 2O = C_6H_5.N(CH_3).N{:}N.N(CH_3).C_6H_5 + 2H_2O.$$

They are solids which undergo decomposition when fused or boiled with dilute acids.

Dimethyl-diphenyl Tetrazone, $C_6H_5.N(CH_3)N_2.N(CH_3).C_6H_5$, crystallizes in leaflets, melting at 133°. The diethyl derivative melts at 108°. The *tetraphenyl* compound, from a-diphenylhydrazine, melts at 123°, and is colored blue by concentrated acids.

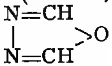
Acid Derivatives of Phenylhydrazine, or Hydrazides :—

$C_6H_5.NH.NH.CO.CH_3$	and	$C_6H_5.N(CO.CH_3).NH_2$.
a-Acetyl Hydrazine.		β-Acetyl Hydrazine.

The a-compounds are obtained by the action of free acids, acid chlorides, acid anhydrides and acid esters upon phenylhydrazine.

Free acids (especially the polyhydric oxy-acids), as well as the lactones, react directly upon digesting them in an acetic-acid solution (*Berichte*, 22, 2728). The hydrazides of the monobasic acids are mostly readily soluble in hot water (p. 489), but the dihydrazides of the polybasic acids dissolve with difficulty. Boiling alkalies and baryta water decompose them all with the separation of phenylhydrazine. The hydrazides are distinguished from the hydrazones by the red-violet color that they yield with concentrated sulphuric acid and a little ferric chloride (Reaction of Bülow, *Annalen*, 236, 195; *Berichte*, 23, 3385).

a-**Formyl-hydrazine**, $C_6H_5.NH.NH.CHO$, melts at 140°; a-**acetyl-hydrazine**, at 128°. a-**Benzoyl-hydrazine** melts at 168°; mercuric oxide oxidizes it to benzoyl-diazo-benzene, $C_6H_5.N{:}N.CO.C_6H_5$ (*Berichte*, 19, 1203). The structure of a-benzoyl hydrazine is proven by the methyl derivative of benzoyl- and dibenzoyl-hydrazine (*Berichte*, 18, 1739). The *β-phenyl hydrazides* are formed when acid chlorides or anhydrides act upon sodium phenylhydrazine (*Berichte*, 22, Ref. 665). β-**Benzoyl-hydrazine**, $C_6H_5.N(CO.C_6H_5).NH_2$, melts at 70°.

Phosgene converts the a-phenyl hydrazides into *carbizine* derivatives (*Berichte*, 21, 2456). These, probably, contain the "ring-shaped" *biazole chain*,  $\left.\begin{array}{l}N{=}CH\\ |\\ N{=}CH\end{array}\right>O$ (*Berichte*, 23, 2821). Carbon disulphide produces *thio-carbizines*, derivatives of *thio-biazole*, $C_2H_2N_2S$.

SO_2 converts phenylhydrazine into hydrazides of sulphurous acid, $C_6H_5.N_2H_3.SO_2$ and $(C_6H_5.N_2H_3)_2SO_2$ (*Berichte*, 23, 475).

Homologous Phenylhydrazines.

o-**Tolyl-hydrazine**, $C_6H_4(CH_3).NH.NH_2$, from orthotoluidine, crystallizes in shining leaflets melting at 59°. When digested with sulphuric acid, it becomes a sulpho-acid, $C_6H_3(CH_3)(N_2H_3).SO_3H$; the sulpho-group occupies the para-position with reference to the hydrazine-group (*Berichte*, 18, 3175; 19, Ref. 301).

p-**Tolyl-hydrazine**, $C_6H_4(CH_3).NH.NH_2$, from para-toluidine, melts at 61°, and distils about 242°. When digested with sulphuric acid, it changes to a basic compound (*Berichte*, 19, Ref. 837).

SULPHO-COMPOUNDS.

The following are representatives of this class of derivatives:—

Benzene Sulphonic Acid,	$C_6H_5.SO_3H$.
" Sulphinic "	$C_6H_5.SO_2H$.
" Sulphone,	$(C_6H_5)_2SO_2$.
" Disulphoxide,	$(C_6H_5)_2S_2O_2$.
" Sulphoxide,	$(C_6H_5)_2SO$.

The *sulphonic acids* of the benzene hydrocarbons (as well as of all other benzene derivatives) are very easily obtained by mixing (or digesting) the latter with concentrated or fuming sulphuric acid. The fatty acids yield like products with more difficulty (pp. 152 and 261):—

$$C_6H_6 + SO_4H_2 = C_6H_5.SO_3H + H_2O,$$
$$C_6H_6 + 2SO_4H_2 = C_6H_4(SO_3H)_2 + 2H_2O.$$

Chlorsulphonic acid, $Cl.SO_2.OH$ (*Berichte*, 18, 2172), acts similarly to sulphuric acid. With it we can obtain the trisulpho-acids (*Berichte*, 15, 307). Further, some sulphonic acids can be obtained from the diazo-amido-derivatives by means of sulphurous acid (p. 635 and *Berichte*, 10, 1715).

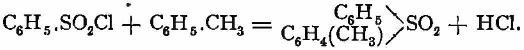
The chloranhydrides of the sulphonic acids, *e. g.*, $C_6H_5.SO_2Cl$, are produced by letting PCl_5 act on the acids, or $POCl_3$ upon the salts. Ammonia converts these into sulphamides, $C_6H_5.SO_2.NH_2$, and zinc and hydrochloric acid will reduce them to sulphydrates (thio-phenols) (p. 152):—

$$C_6H_5.SO_2Cl + 3H_2 = C_6H_5.SH + 2H_2O + HCl.$$

The *sulphinic acids* of benzene, with the structure $C_6H_5.SO.OH$ or $\begin{matrix}C_6H_5\\H\end{matrix}\!\!>SO_2$ are perfectly analogous to those of the fatty series (p. 154). They are best prepared by the action of zinc dust upon the ethereal solutions of the sulphonic chlorides (*Berichte*, 13, 1273). They also result in the action of SO_2 upon benzene in the presence of $AlCl_3$ (*Berichte*, 20, 195):—$C_6H_6 + SO_2 = C_6H_5.SO_2H$.

The *real esters* of these acids, $C_6H_5.SO.O.C_2H_5$, are formed by the action of chlorcarbonic esters upon sulphinates (p. 154), and by the etherification of the free sulphinic acids with alcohol and HCl (*Berichte*, 18, 2506; 19, 1224). The esters are not very stable; alkalies saponify them, yielding sulphinates and alcohol, etc. The *sulphones*, their isomerides, *e. g.*, $(C_6H_5)_2SO_2$, diphenyl-sulphone (p. 142), are obtained by the action of SO_3 (or chlorsulphonic acid, $ClSO_3H$) upon benzenes (together with sulphonic acids): $2C_6H_6 + SO_3 = (C_6H_5)_2SO_2 + H_2O$.; by the distillation of sulphonic acids (together with benzenes), and by the oxidation of the phenyl sulphides, *e.g.*, $(C_6H_5)_2S$, with nitric acid.

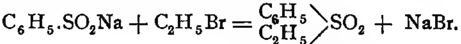
The benzene sulphones are formed synthetically on heating sulphonic acid with benzene and P_2O_5:$C_6H_5.SO_3H + C_6H_6 = C_6H_5.SO_2.C_6H_5 + H_2O$; further, by the action of zinc dust or aluminium chloride upon a mixture of the sulphonic chlorides and benzenes; *mixed* sulphones are also produced in this manner:—



$$C_6H_5.SO_2Cl + C_6H_5.CH_3 = \begin{matrix} C_6H_5 \\ C_6H_4(CH_3) \end{matrix}\!\!>SO_2 + HCl.$$

The same phenyl tolyl-sulphone results from benzene sulphonic acid and toluene as from toluene-sulphonic acid and benzene, which would prove *that both groups are in union with sulphur* and *that the latter is sexivalent* (*Berichte*, 11, 2181).

Mixed sulphones, containing alkyls, are prepared from the sodium sulphinates by the action of the alkylogens (p. 142):—



$$C_6H_5.SO_2Na + C_2H_5Br = \begin{matrix} C_6H_5 \\ C_2H_5 \end{matrix}\!\!>SO_2 + NaBr.$$

Phenyl-ethyl-sulphone.

The *benzene-thiosulphonic acids* are formed when alkaline sulphides act upon the chlorides of the sulphonic acids:—

$$C_6H_5.SO_2Cl + K_2S = C_6H_6.SO_2.SK + KCl.$$

Potassium Benzene-thio-sulphonate.

And by acting on these salts with alkylogens, esters of the thio-sulphonic acids (the disulphoxides) will be produced (*Berichte*, 20, 2079):—

$$C_6H_5.SO_2.SK + C_2H_5I = C_6H_5.SO_2.S.C_2H_5 + KI.$$

These are identical with the so-called alkyl-disulphoxides (p. 154).

Phenyl esters, *e. g.*, $C_6H_5.SO_2.S.C_6H_5$, are obtained by oxidizing the thiophenols with nitric acid and by heating the sulphinic acids with water. (*Berichte*, 18, 2500). Alkalies and alkaline sulphides saponify them (p. 154 and *Berichte*, 19, 3131).

The benzene sulphoxides are produced by the action of SO_2 or SO_2Cl_2 upon benzenes in the presence of $AlCl_3$ (*Berichte*, 20, 191):—

$$2C_6H_6 + SOCl_2 = (C_6H_5)_2SO + 2HCl.$$

The benzene sulphonic acids are perfectly analogous to those of the fatty series. They are very stable and are not decomposed on boiling with alkalies. They yield phenols when fused with alkalies:—

$$C_6H_5.SO_3K + KHO = C_6H_5.OH + SO_3K_2.$$

When distilled with potassium cyanide (or dry yellow prussiate of potash) nitriles result:—

$$C_6H_5.SO_3K + CNK = C_6H_5.CN + SO_3K_2.$$

Amido-compounds are produced when sodium amide acts upon benzene sulphonates (*Berichte*, 19, 903):—

$$C_6H_5.SO_3Na + NH_2Na = C_6H_5.NH_2 + SO_3Na_2.$$

Hydrocarbons (together with phenyl sulphones) are formed when the free acids are subjected to distillation:—

$$C_6H_5.SO_3H = C_6H_6 + SO_3.$$

This rupture is more easily accomplished by heating the acids with concentrated HCl to 150°, or by distilling the ammonium salt of the sulphonic acid, or a mixture of the lead salt with ammonium chloride (*Berichte*, 16, 1468). The decomposition results with least difficulty by conducting steam into the dry sulpho-acid, or its solution in concentrated sulphuric acid; superheated steam is most effective (*Berichte*, 19, 92).

The sulphonic acids of the substituted hydrocarbons are obtained either by the action of sulphuric acid on the substituted hydrocarbons, or by the substitution of the sulphonic acids. In nitration the sulpho-group is often replaced by the nitro-group, just as on heating with PCl_5 it is sometimes substituted by chlorine:—

$$C_6H_4Cl.SO_2Cl + PCl_5 = C_6H_4Cl_2 + PCl_3O + SOCl_2.$$

Most of the substituted benzene sulphonic acids have their sulpho-group replaced by hydrogen if they are heated to 150-200° with concentrated hydrochloric acid:—

$$C_6H_4Br.SO_3H + H_2O = C_6H_5Br + SO_4H_2.$$

Nitro-benzenes and amido-benzenes result in like manner from the nitro-benzene- and amido-benzene-sulphonic acids (*Berichte*, 10, 317). Chlorine and bromine occasionally effect a like replacement of the sulpho-group (*Berichte*, 16, 617).

The brominated benzene-sulphonic acids can form sulpho-anhydrides, *e. g.*, $\begin{matrix}C_6H_3Br_2.SO_2\\C_6H_3Br_2.SO_2\end{matrix}\!>\!O$. They result from the action of pyrosulphuric acid, $(SO_2)_2O(OH)_2$, upon brombenzenes (*Berichte*, 16, 653).

The *sulphinic acids* are not very stable, and when heated or allowed to stand some time over sulphuric acid they split up into sulphonic acids and *disulphoxides* (*Berichte*, 18, 2500).

The air and oxidizing agents (especially BaO_2) convert them into sulphonic acids. Their salts unite with sulphur, forming thio-sulphonates. When fused, they decompose into benzenes and alkaline sulphites:—

$$C_6H_5.SO_2K + KOH = C_6H_6 + SO_3K_2.$$

Benzene-sulphonic Acid, $C_6H_5.SO_3H$. For its preparation equal parts of benzene and ordinary sulphuric acid are boiled for some time; or benzene is shaken with fuming sulphuric acid. Afterwards dilute with water and saturate with barium or lead carbonate. The free sulphonic acid is separated from its salts by means of sulphuric acid or hydrogen sulphide.

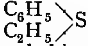
Benzene sulphonic acid crystallizes in small plates, $C_6H_5 SO_3H + 1\frac{1}{2}H_2O$, which are readily soluble in alcohol and water, and deliquesce in the air. In its dry distillation the acid yields benzene and phenylsulphone (in slight quantity), and when fused with caustic potash phenol is produced.

The *barium salt*, $(C_6H_5.SO_3)_2Ba + H_2O$, forms pearly leaflets, and is sparingly soluble in alcohol. The *zinc salt*, $(C_6H_5.SO_3)_2Zn + 6H_2O$, crystallizes in six-sided plates.

Benzene-sulpho-chloride, $C_6H_5.SO_2Cl$, is an oil, insoluble in water, but dissolved by alcohol and ether. Its specific gravity at 23° is 1.378. It is crystalline below 0°, and boils at 247° with decomposition. It slowly reverts to the acid upon boiling with water. It may be obtained by gently digesting $C_6H_5.SO_3Na$ with PCl_5 and treating the product with water. If the chloride be digested with ammonia or ammonium carbonate we obtain—

Benzenesulphamide, $C_6H_5.SO_2.NH_2$, which crystallizes from alcohol in pearly laminæ. It melts at 149° and sublimes. From the alcoholic solution silver nitrate precipitates $C_6H_5.SO_2.NHAg$. The amide hydrogen can also be replaced by acid or alcohol radicals.

Benzene Sulphinic Acid, $C_6H_5.SO_2H$ (its zinc salt), is obtained by the action of zinc dust upon benzene sulphochloride. It crystallizes from hot water in large, brilliant prisms, and dissolves readily in alcohol and ether. It melts at 69°, and decomposes at 100°. In the air it oxidizes readily to benzene sulphonic acid. The *silver salt*, $C_6H_5.SO_2Ag$, is sparingly soluble in water.

Phenyl Ethyl Sulphone, $C_6H_5.SO_2.C_2H_5$, is formed in the oxidation of phenyl-ethyl-sulphide,  $\begin{matrix}C_6H_5\\C_2H_5\end{matrix}\Big>S$, with potassium permanganate, and from sodium benzene sulphinate with ethyl bromide (p. 660). It melts at 42° and boils above 300°. Isomeric benzene-sulphinic ester, $C_6H_5.SO.O.C_2H_5$, is only known in mixtures (p. 659).

Di-phenylsulphone, $(C_6H_5)_2SO_2$, Benzene Sulphone, Sulphobenzide, is formed by the distillation of benzene sulphonic acid, and by the oxidation of phenyl sulphide, $(C_6H_5)_2S$; further, from benzene sulphonic chloride, $C_6H_5.SO_2Cl$, and mercury diphenyl. It is also obtained by the action of fuming sulphuric acid, or SO_3 upon benzene. It dissolves with great difficulty in water and crystallizes from alcohol in plates. It melts at 128–129°, and distils without decomposition. It is converted into benzene-sulphonic acid when digested with concentrated sulphuric acid:—

$$(C_6H_5)_2SO_2 + SO_4H_2 = 2C_6H_5.SO_3H.$$

When heated with PCl_5, or in a current of chlorine gas, it is decomposed according to the equation:—

$$(C_6H_5)_2SO_2 + Cl_2 = C_6H_5Cl + C_6H_5.SO_2Cl.$$

C_6H_5Cl and its addition products are also formed when chlorine acts upon it in sunlight.

Benzene disulphoxide, $(C_6H_5)_2S_2O_2$ (p. 659), is produced along with benzene sulphonic acid on heating benzene sulphinic acid with water to 130°. It crystallizes in shining needles, and melts at 130°. It is insoluble in water but is readily dissolved by alcohol and ether.

Ethylene Diphenyl-disulphone, $\begin{array}{l}CH_2.SO_2.C_6H_5\\ |\\ CH_2.SO_2.C_6H_5\end{array}$ (p. 307), is obtained from ethylene bromide and sodium benzene sulphinate. When heated with alkalies, it breaks down into benzene sulphinic acid and *phenylsulphone-ethyl alcohol,* $C_6H_5.SO_2.CH_2.CH_2.OH$; chromic acid oxidizes this to phenylsulphone-acetic acid, $C_6H_5.SO_2.CH_2.COOH$ (*Berichte,* 18, 155). The latter compound and its esters are obtained from sodium phenylsulphinate by the action of chloracetic acid. The hydrogen of the CH_2-group in the ester is, indeed, replaceable by sodium, but *not* by alkyls (*Berichte,* 22, 1447; 23, 1647).

See *Berichte,* 23, 752, 1409, for analogous *di-* and *tri-sulphones,* as well as their decompositions, etc.

a- and *β*-**Phenyl-sulpho-propionic Acids,** $C_6H_5.SO_2.CH(CH_3).CO_2H$, have been prepared in a similar manner (*Berichte,* 21, 89).

Benzene-disulphonic Acids, $C_6H_4\langle\begin{array}{l}SO_3H\\ SO_3H\end{array}$. On heating benzene with fuming sulphuric acid to 200° C., we get *meta-* and *para*-benzene disulphonic acids, with the former in predominating quantity, but by prolonged heating it passes into the *para*-variety (*Berichte,* 9, 550). They can be separated by means of their potassium salts. *Meta*-disulphonic acid (1, 3) is produced by heating parabrombenzenesulphonic acid with sulphuric acid to 220° and displacing the bromine with sodium amalgam, or from disulphanilic acid (p. 666) by means of the diazo-compound.

Orthobenzene disulphonic acid (1, 2) is formed from meta-amido benzene sulphonic acid by further introduction of the sulpho-group, and replacement of NH_2. The melting points of the sulphochlorides and sulphamides of the three isomeric disulphonic acids are:—

	Ortho.	Meta.	Para.
$C_6H_4(SO_2Cl)_2$	105°	63°	132°
$C_6H_4(SO_2NH_2)_2$	233°	229°	288°.

The corresponding *dicyanides,* $C_6H_4(CN)_2$ (see nitriles), are obtained by distillation with potassium cyanide or potassium ferrocyanide. When fused with potassium hydroxide, both *meta* and *para* acids yield resorcinol (metadioxybenzene); at lower temperatures metaphenol-sulphonic acid, $C_6H_4(OH)\,SO_3H$, results at first from both acids.

Benzene-trisulphonic Acid, $C_6H_3(SO_3H)_3$ (1, 3, 5), is easily made by heating potassium *m*-benzene disulphonate with common sulphuric acid (*Berichte,* 21, Ref. 49). The free acid (from the lead salt) crystallizes in long needles with $3H_2O$; its *chloride* melts at 184°; its *amide* at 306°. Fused with caustic potash it yields phloroglucin, $C_6H_3(OH)_3$, and upon heating with potassium cyanide it forms the nitrile, which upon saponification becomes trimesic acid, $C_6H_3(CO_2H)_3$.

The Chlorbenzene-sulphonic Acids, $C_6H_4Cl.SO_3H$, are obtained from the three amidobenzene-sulphonic acids, by treating their diazo-compounds with hydrochloric acid. The (1, 4)-acid is also produced in the action of SO_4H_2 upon $C_6H_5.Cl$. The *amide* of the (1, 2)-acid melts at 182°; the *amide* of (1, 3)-acid at 148°; that of the (1, 4)-acid at 143°. The *chloride* of the (1, 4)-acid, $C_6H_4Cl.SO_2Cl$, melts at 51°; it yields (1, 4)-$C_6H_4Cl_2$, when heated with PCl_5.

The Brombenzene-sulphonic Acids, $C_6H_4Br.SO_3H$, are obtained like the chlor-acids. The (1, 4)-acid is also formed on heating C_6H_5Br with SO_4H_2 or SO_3HCl; the (1, 3)-acid by heating benzenesulphonic acid with bromine to 100°, or by the action of Br upon $C_6H_5SO_3Ag$ at ordinary temperatures. They are very deliquescent, crystalline bodies; the para-acid melts at 88°. All three yield resorcinol (1, 3), when they are fused with KOH. They form *dicyanides*, $C_6H_4(CN)_2$, by distilling their potassium salts with potassium cyanide or dry yellow prussiate of potash. Dicarboxylic acids are obtained from these.

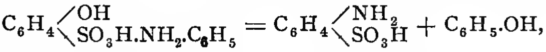
Nitrobenzene-sulphonic Acids, $C_6H_4(NO_2).SO_3H$. If nitrobenzene be dissolved in fuming sulphuric acid, or benzene sulphonic acid in concentrated nitric acid, the three nitrobenzene sulphonic acids are produced—the (1, 4)-acid in largest quantity. For their separation they are converted into the amides, $C_6H_4(NO_2).SO_2.NH_2$, which are then distilled. The free acids are very deliquescent crystalline masses. Their *chlorides* melt as follows: (1, 2) at 67°; (1, 3) at 60°; (1, 4) is a liquid. The *amides* fuse: (1, 2) at 186°; (1, 3) at 161°; (1, 4) at 131°. Ammonium sulphide reduces them to the corresponding amidobenzene sulphonic acids.

Amidobenzene-sulphonic Acids, $C_6H_4(NH_2).SO_3H$. They are produced by the reduction of the three nitrobenzene sulphonic acids with ammonium sulphide.

The para-acid, commonly called *sulphanilic acid*, is obtained by heating aniline (1 part) with fuming sulphuric acid (2 parts) to 180° until SO_2 appears. On diluting with water, the acid separates as a crystalline mass. Its diazo-compounds are changed by hydrobromic acid into the corresponding brombenzene-sulpho acids; by hydrochloric acid into chlorbenzene sulphonic acids.

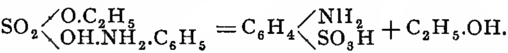
The three amido-benzene sulphonic acids dissolve with difficulty in water, alcohol and ether. The (1, 2)-acid either crystallizes in anhydrous rhombohedra, or in four-sided prisms containing ½H_2O; these do not effloresce. The (1, 3)-acid crystallizes in delicate needles or in prisms with 1½H_2O, which effloresce. The sodium amido-benzene-sulphonates yield acetyl derivatives with acetic anhydride (*Berichte*, 17, 708).

Sulphanilic Acid (1, 4) is obtained by heating (1, 4)-and (1, 2)-aniline-phenol-sulphonate:—



$$C_6H_4\left\langle\begin{array}{l}OH\\SO_3H.NH_2.C_6H_5\end{array}\right. = C_6H_4\left\langle\begin{array}{l}NH_2\\SO_3H\end{array}\right. + C_6H_5.OH,$$

or aniline ethyl sulphate to 200°:—



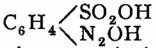
$$SO_2\left\langle\begin{array}{l}O.C_2H_5\\OH.NH_2.C_6H_5\end{array}\right. = C_6H_4\left\langle\begin{array}{l}NH_2\\SO_3H\end{array}\right. + C_2H_5.OH.$$

It yields aniline and not amidophenol when fused with caustic potash. It crystallizes from hot water in rhombic plates with 1 molecule H_2O; these effloresce in the air. They are soluble in 112 parts H_2O at 15° (*Berichte*, 14, 1933). It yields a considerable quantity of quinone, when oxidized with MnO_2 and H_2SO_4 or chromic acid.

For nitro-aniline-sulphonic acids, consult *Berichte*, 21, 2579, 3220; 22, 847.

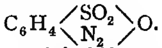
Phenylsulphaminic Acid, $C_6H_5.NH.SO_3H$ (p. 164), is isomeric with the amidobenzene-sulphonic acids. It results from the action of chlorsulphonic acid upon aniline. Its salts are very stable; boiling water does not decompose them. Boiling water containing a little acid, readily decomposes the free acid into aniline and sulphuric acid (*Berichte*, 23, 1653).

Nitrous acid transforms the three amido-benzene-sulphonic acids into the anhydrides of the *diazobenzene-sulphonic acids* (p. 630):—



$$C_6H_4\left<\begin{matrix}SO_2OH\\N_2OH\end{matrix}\right.$$

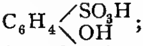
Diazobenzene-sulphonic Acid.



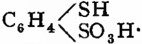
$$C_6H_4\left<\begin{matrix}SO_2\\N_2\end{matrix}\right>O.$$

Anhydride.

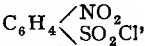
The hydrous sulpho-acids are not known; they pass at once into anhydrides. It is rather remarkable that, while otherwise it is only the ortho-compounds of the benzene derivatives which form inner anhydrides (p. 351), all three of the diazobenzene sulpho-acids are capable of anhydride formation.

p-Diazobenzene-sulphonic acid (its anhydride) is obtained by dissolving sulphanilic acid in sodium hydroxide, adding an equivalent quantity of sodium nitrite and pouring the mixture into dilute sulphuric acid. The acid separates in needles that dissolve with difficulty. It exhibits all of the reactions of the diazo-compounds. When heated to 80° with water, the diazo-acid becomes *p*-phenol-sulphonic acid,  $C_6H_4\left<\begin{matrix}SO_3H\\OH\end{matrix}\right.$; heated with absolute alcohol, it forms benzene-sulphonic acid. It is used in the preparation of various azo-dyes.

m-Diazobenzene-sulphonic acid, Metanilic acid (p. 664), unites with diphenylamine to yield *metanilic yellow*.

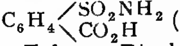
The action of the diazo-sulphonic acid upon alcoholic H_2S, is to substitute the diazo-group by SH, with the production of the phenolsulphonic acids, *e. g.*,  $C_6H_4\left<\begin{matrix}SH\\SO_3H\end{matrix}\right.$.

The benzene-diazo-sulphonic diazoamido-derivatives (the same as those of benzene carboxylic acids) are not known.

The action of HI upon the nitro-benzene-sulphonic chlorides,  $C_6H_4\left<\begin{matrix}NO_2\\SO_2Cl\end{matrix}\right.$, produces the *sulphimido benzenes*, which are nitrodiphenyl disulphides (*Berichte*, 21, 1099).

Disulphanilic Acid, $C_6H_3(NH_2)(SO_3H)_2$ (1, 4, 2 — NH_2 in 1), is obtained by protracted heating of sulphanilic acid to 180° with concentrated sulphuric acid. The replacement of the amido-group produces metabenzene-disulphonic acid (p. 663).

Toluene Sulphonic Acids, $C_6H_4(CH_3).SO_3H$. It is chiefly the para-compound, together with some ortho- and meta- (*Berichte*, 17, Ref. 283), which is produced by the solution of toluene in sulphuric acid or by the action of chlorsulphonic acid upon it. The *chloride* of the *para*-acid is solid and melts at 69°; that of the ortho-acid is liquid. When fused with alkali the para-acid yields paracresol and para-oxybenzoic acid, the ortho-acid, however, ortho cresol and salicylic acid. When the former is oxidized with a chromic-acid mixture, it forms parasulphobenzoic acid, while the latter passes into ortho-sulphobenzoic acid (*Berichte*, 20, 2929).

Ammonium carbonate converts the three sulphochlorides into three *toluenesulphamides*, $C_6H_4(CH_3).SO_2.NH_2$ (*Berichte*, 21, Ref. 100). Potassium permanganate oxidizes these to the corresponding sulphamine benzoic acids,  $C_6H_4\left<\begin{matrix}SO_2NH_2\\CO_2H\end{matrix}\right.$ (*Berichte*, 21, 242).

Toluene Disulphonic Acids, $C_6H_3(CH_3)(SO_3H)_2$. The six possible isomerides are known (*Berichte*, 20, 350).

PHENOLS.

The mono-, di- and tri-hydric phenols are derived by the replacement of hydrogen in the benzenes by hydroxyls:—

$C_6H_5.OH$	$C_6H_4(OH)_2$	$C_6H_3(OH)_3$.
Phenol.	Dioxybenzenes.	Trioxybenzenes.

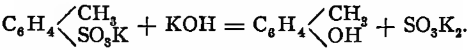
The phenols correspond to the tertiary alcohols, as they yield neither acids nor ketones upon oxidation. Their acid nature, distinguishing them from alcohols, is governed by the more negative nature of the phenyl group (p. 557). The following are the more general and most important methods of forming them:—

1. By the action of nitrous acid upon the aqueous solution of the amido-compounds, or by decomposing the diazo-derivatives with boiling water (p. 632).

The sulphuric acid salts of the diazo-compounds are particularly well adapted to this end; the nitric acid salts tend to yield nitro-phenols. It is best to dissolve the amido-derivatives in dilute sulphuric acid (2 equivalents), add aqueous potassium nitrite (1 molecule), and boil the strongly diluted solution until the disengagement of nitrogen ceases.

2. Fusion of the sulphonic acids with potassium or sodium hydroxide:—

$$C_6H_5.SO_3K + KOH = C_3H_6.OH + SO_3K_2,$$



$$C_6H_4\left\langle\begin{matrix}CH_3\\SO_3K\end{matrix}\right. + KOH = C_6H_4\left\langle\begin{matrix}CH_3\\OH\end{matrix}\right. + SO_3K_2.$$

Here the sulpho-group disappears as a sulphite (p. 152).

The experiment is executed in a silver dish at higher or lower temperatures, the fusion supersaturated with sulphuric acid, and the phenol extracted by shaking with ether.

In fusing sulphonic acids or phenols containing halogens, the latter are also replaced with formation of polyhydric phenols:—

$$C_6H_4.Cl.SO_3K + 2KOH = C_6H_4(OH)_2 + SO_3K_2 + KCl,$$
$$C_6H_4Cl.OH + KOH = C_6H_4(OH)_2 + KCl.$$

Occasionally the sulpho-group splits off as sulphate and is replaced by hydrogen; thus, cresolsulphonic acid yields cresol.

3. Small quantities of phenol can be obtained from benzene by the action of ozone, hydrogen peroxide (palladium hydride and water), and by shaking with sodium hydroxide and air (*Berichte*, 14, 1144).

4. The halogen benzene substitution products do not react with alkalies; but if nitro-groups are present at the same time, the halogens are replaced even by digesting with aqueous alkalies—this will occur the more readily if the nitro-groups be multiplied. For ex-

ample, ortho- and para-chlornitro-benzene (but not meta) yield the corresponding nitro-phenols (p. 676), when they are heated to 120° with sodium hydroxide; the dinitro-chlorbenzenes even react when boiled with carbonates, and the trinitro-chlorbenzene even with water.

p-Nitrophenol-ethers, $C_6H_4(NO_2).OR$, are produced on boiling *p*-chlornitrobenzene with caustic soda and 60 per cent. alcohol; if absolute alcohol be applied there is simultaneous reduction and formation of chlorazobenzene (*Berichte*, 15, 1005).

The amide-group in the nitroamido-derivatives can also be replaced by hydroxyl on boiling with aqueous alkalies; ortho- and para-nitranilines, $C_6H_4(NO_2).NH_2$ (not meta), yield their corresponding nitrophenols. The ortho-dinitro-products react similarly (p. 587).

5. The dry distillation of salts of the oxy-acids of the benzene series with lime (p. 570):—

$$\underset{\text{Oxybenzoic Acid.}}{C_6H_4(OH).CO_2H} = \underset{\text{Phenol.}}{C_6H_5.OH} + CO_2,$$

$$\underset{\text{Gallic Acid.}}{C_6H_2(OH)_3.CO_2H} = \underset{\text{Pyrogallol or Pyrogallic Acid.}}{C_6H_3(OH)_3} + CO_2.$$

6. Dry distillation of various complex carbon compounds, *e. g.*, wood and coal. To isolate the phenols from the coal tar, shake the fraction boiling at 150–209°, with aqueous potash, separate the aqueous solution from the oil containing the hydrocarbons, and saturate it with hydrochloric acid. The separated phenols are purified by fractional distillation.

Wood-tar oils (*creasote*) consist of a mixture of different phenols and their ethers; the portion, boiling at 180-300°, contains phenol, $C_6H_5.OH$, para-cresol, $C_6H_4(CH_3).OH$, phlorol, $C_6H_3(CH_3)_2.OH$, also guaiacol, $C_6H_4(O.CH_3).OH$, creosol, $C_6H_3(CH_3).(O.CH_3).OH$, and the dimethyl ether of pyrogallic acid, $C_6H_3(OH)_3$, and methyl- and propyl pyrogallol (*Berichte*, 14, 2005).

7. The synthesis of the higher phenols by introduction of alkyls into the benzene nucleus (p. 570) takes place readily on heating the phenols with alcohols and $ZnCl_2$ to 200° (*Berichte*, 14, 1842; 17, 669):—

$$C_6H_5.OH + C_2H_5.OH = C_6H_4(C_2H_5).OH + H_2O.$$

Alkyl ethers of the phenols are simultaneously produced; methyl alcohol yields methyl-phenol, $C_6H_5.O.CH_3$. Magnesium chloride (*Berichte*, 16, 792) and primary alkali sulphates (*Berichte*, 16, 2541) possess the same condensing power as $ZnCl_2$. Phenol and resorcinol condense to ketones, *e. g.*, dioxybenzophenone, $C_6H_4(OH).CO.C_6H_4.OH$ (*Berichte*, 16, 2298), when heated with salicylic acid and tin chloride.

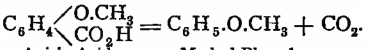
8. Many benzene derivatives are transposed in the animal organism into phenols; thus, benzene yields phenol; brombenzene, bromphenol; aniline, amidophenol and phenol hydroquinone. Different phenols are found already formed as phenol sulphuric acids (p. 670) in the urine of mammals.

The phenols are the analogues of the tertiary alcohols, but possess a more acid character (p. 666). The hydrogen of their hydroxyl can be readily substituted by metals, by the action of bases, chiefly of the alkalies. Carbon dioxide separates the phenols again from these salts. The entrance of negative groups into the benzene nucleus increases the acid nature of the phenols. Thus trinitrophenol manifests the properties of an acid, as it decomposes carbonates. The hydroxyl-hydrogen of the phenols can also be replaced by alcohol and acid radicals.

The *alcohol-ethers* are formed: by the action of the alkyl iodides upon the salts of the phenols (chiefly the silver salts), or by heating a mixture of the alkali salts of the phenols with an excess of alkyl sulphates, in aqueous or alcoholic solution (*Berichte*, 19, Ref. 139):—

$$C_6H_5.OH + C_2H_5.I + KOH = C_6H_6.O.C_2H_5 + KI + H_2O;$$

and by the dry distillation of the phenol ethers of the oxy-acids with lime:—



$$C_6H_4\begin{cases}O.CH_3\\CO_2H\end{cases} = C_6H_5.O.CH_3 + CO_2.$$

Anisic Acid. Methyl Phenol.

Boiling alkalies do not alter the alcohol ethers. When, however, they are heated with hydriodic or hydrochloric acid, they split up into their components:—

$$C_6H_5.O.CH_3 + HI = C_6H_5.OH + CH_3I.$$

The *acid esters* are obtained by acting with acid chlorides or anhydrides upon the phenols or their salts; also by digesting the phenols with acids and $POCl_3$. On boiling with alkalies or even with water, they, like all esters, break down into their components.

To effect the substitution of all the hydroxyl-hydrogen atoms in the polyhydric phenols by acetyl groups, it is recommended to heat them with acetic anhydride and sodium acetate.

Phosphorus sulphide converts the phenols into thio-phenols:—

$$5C_6H_5.OH + P_2S_5 = 5C_6H_5.SH + P_2O_5.$$

The phosphorus haloids replace the hydroxyls of the phenols by halogens, forming substituted benzenes. When heated with zinc dust the phenols are reduced to hydrocarbons. The anilines result on heating with zinc-ammonium chloride (compare p. 593).

On adding phenols (mono- or polyhydric) to a solution of KNO_2 (6 per cent.) in concentrated sulphuric acid, intense colorations arise; with common phenol we get first a brown, then green, and finally a royal-blue color (Reaction of Liebermann) (see *Berichte*, 17, 1875). Dyes are produced in this manner; their character is as yet unexplained. They have been called dichroïnes (*Berichte*, 21, 249). The phenols afford similar colors in the presence of sulphuric acid, with diazo-compounds, and nitroso-derivatives (p. 636). Ferric chloride imparts color to the solutions of most phenols. Mercury nitrate, containing nitrous acid, colors nearly all the phenols red (Reaction of Plugge) (*Berichte*, 23, Ref. 202).

The hydrogen of the benzene residue in phenols can be replaced, further, by the halogens and groups NO_2, SO_3H, etc. In the alcohol-ethers of the nitro-phenols (as with the acid esters) we can replace the OH by NH_2, on heating with alcoholic ammonia (p. 593):—

$$C_6H_4(NO_2).O.CH_3 + NH_3 = C_6H_4(NO_2).NH_2 + CH_3.OH.$$

The phenols and their halogen products may be converted into oxy-acids by the action of sodium and carbon dioxide (see aromatic series):—

$$C_6H_5.OH + CO_2 = C_6H_4(OH).CO_2H.$$

Oxyaldehydes, $C_6H_4(OH).CHO$, are produced from phenols, chloroform and caustic soda, and oxyacids (see these) from phenols and carbon tetrachloride. The diazo- yield azo-compounds with phenols—the tropæoline dyes belong to this class (p. 644). Dyestuffs belonging to the aurine series, and derived from triphenylmethane, $CH(C_6H_6)_3$ (see this), are obtained from the phenols by their action upon benzotrichloride, $C_6H_5.CCl_3$. The so-called phthaleïns are combinations of phthalic acid and the phenols.

MONOHYDRIC PHENOLS.

Phenol, $C_6H_5.OH$.
Cresols, $C_6H_4.CH_3(OH)$.
Xylenols, $C_6H_3(CH_3)_2.OH$, etc.

Phenol, $C_6H_5.OH$ (Benzene Phenol, Carbolic Acid, Creasote). This was first discovered (1834) in coal-tar, by Runge. It is obtained from amidobenzene, from benzene-sulphonic acid, from the three oxy-benzoic acids, etc., by the methods previously described. It occurs already formed in *Castoreum* and in the urine of the herbivoræ.

Commercial phenol is a colorless crystalline mass, which gradually acquires a reddish color, and deliquesces on exposure to the air. Pure phenol crystallizes in long, colorless prisms, melts at 42°, and boils at 183°; its specific gravity at 0° is 1.084. It possesses a characteristic odor, burning taste, and poisonous and antiseptic properties. It dissolves in 15 parts water at 20°, and very readily in alcohol, ether and glacial acetic acid. Ferric salts impart a violet color to its neutral solutions. Bromine water precipitates tribromphenol from even very dilute solutions. Diphenols, $C_{12}H_8(OH)_2$, derivatives of diphenyl (see this), are produced on fusing phenol with caustic potash.

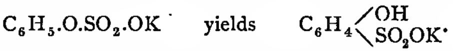
Potassium Phenylate or *Phenoxide*, $C_6H_5.OK$, is obtained by dissolving phenol in potassium hydroxide. It crystallizes in delicate, readily soluble needles. CO_2 separates phenol from it, which, therefore, is insoluble in alkaline carbonates. Bartya, lime, and litharge form similar compounds.

Phenaceteïn, *Phenacetolin*, $C_{16}H_{12}O_2$ (*Berichte*, 15, 2907), is obtained by heating phenol with acetic acid and zinc chloride. This compound is employed as an indicator in alkalimetry (*Berichte*, 14, 2306).

ACID ESTERS OF PHENOL (p. 668)—ETHEREAL SALTS.

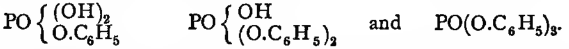
Phenylsulphuric Acid, $C_6H_5.O.SO_3H$, is not known in a free state; when liberated from its salts by concentrated hydrochloric acid, it immediately breaks down into phenol and sulphuric acid. Its *potassium salt*, $C_6H_5.O.SO_3K$, forms leaflets, not very soluble in cold water, and occurs in the urine of herbivorous animals, and also in that of man and the dog after the ingestion of phenol. It is synthetically prepared, like other phenols, on heating potassium phenoxide with an aqueous solution of potassium pyrosulphate (*Berichte*, 9, 1715).

The phenyl sulphuric acids are very stable in aqueous and alkaline solution; upon digesting with mineral acids, however, they are very rapidly decomposed. When potassium phenylsulphate is heated in a tube it passes quietly into *p*-potassium sulphonate:—



$$C_6H_5.O.SO_2.OK \quad \text{yields} \quad C_6H_4\left\langle\begin{matrix}OH\\SO_2OK\end{matrix}\right..$$

The *phenol esters of phosphoric acid* are produced by the action of PCl_5 upon phenol (together with chlorides):—



$$PO\begin{cases}(OH)_2\\O.C_6H_5\end{cases} \qquad PO\begin{cases}OH\\(O.C_6H_5)_2\end{cases} \quad \text{and} \quad PO(O.C_6H_5)_3.$$

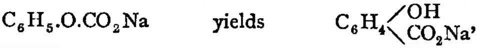
The *triphenyl ester* is easily formed on boiling phenol with phosphorus oxychloride (*Berichte*, 16, 1763). It is crystalline, melts at 45°, and boils near 400°. Distilled with potassium cyanide it yields benzonitrile, $C_6H_5.CN$.

Consult *Berichte*, 18, 1700, upon the phosphoric acid esters of the higher phenols and their conversion into nitriles.

At the ordinary temperature carbon dioxide converts dry sodium phenate (at ordinary pressure) into the sodium salt of *Phenylcarbonic Acid* (*Berichte* 18, Ref. 440):—

$$C_6H_5.ONa + CO_2 = C_6H_5.O.CO_2Na.$$

This is a white hygroscopic powder, decomposed again by water. When heated under pressure to 120–130° sodium salicylate results:—



$$C_6H_5.O.CO_2Na \quad \text{yields} \quad C_6H_4\left\langle\begin{matrix}OH\\CO_2Na\end{matrix}\right.,$$

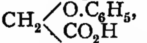
just as phenolsulphonic acid is obtained from phenylsulphuric acid (see above). When heated to 190° with sodium phenate sodium phenyl carbonate yields disodium salicylate and phenol:—

$$C_6H_5.O.CO_2Na + C_6H_5.ONa = C_6H_4(ONa).CO_2Na + C_6H_5.OH.$$

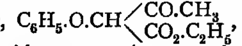
The carbonic acid ester, *Phenyl Carbonate*, $CO(O.C_6H_5)_2$, is produced on heating phenol and phosgene gas, $COCl_2$, to 150°. It is readily obtained by leading phosgene gas into the aqueous solution of sodium phenylate (*Journ. pract. Chem.*, 27, 139, *Berichte*, 17, 287). It crystallizes from alcohol in shining needles, and melts at 78°. It yields sodium salicylate (see this) when heated to 200° with sodium hydroxide. Urea results if it be heated with ammonia, and by using amine bases, instead of ammonia, phenylated ureas will constitute the product (*Berichte*, 23, 694).

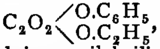
Mixed carbonates containing phenol and alkyls, *e. g.*, phenyl-ethyl carbonate, $CO_3(C_2H_5)(C_6H_5)$, are produced by the action of chlor-formic esters upon the sodium salts of the phenols.

The *acetic ester*, $C_6H_5.O.C_2H_3O$, is obtained by boiling the phosphoric ester with potassium acetate, and is an agreeable-smelling liquid, boiling at 190°.

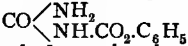
Phenyl-glycollic Acid,  $CH_2{<}\begin{matrix}O.C_6H_5\\CO_2H\end{matrix}$, phenyl oxy-acetic acid (isomeric with mandelic acid), is produced by heating monochloracetic acid with potassium phenate to 150°. Long, silky needles, melting at 96°. All other phenols react analogously.

The action of sodium phenate upon chloracetoacetic ester produces:—

Phenoxyl-acetoacetic Ester,  $C_6H_5.O.CH{<}\begin{matrix}CO.CH_3\\CO_2.C_2H_5\end{matrix}$, a dark oil, that is condensed by sulphuric acid, with water exit, to methylcoumarilic ester. Other coumarilic compounds are analogously produced (see these and *Berichte*, 19, 1291).

Phenyl Ethyl Oxalic Ester,  $C_2O_2{<}\begin{matrix}O.C_6H_5\\O.C_2H_5\end{matrix}$, formed by the action of chlor-oxalic ester (p. 405) upon phenol, is an oil boiling at 236°, and is slowly decomposed by water into phenol, oxalic acid and alcohol.

The *succinic ester*, $C_2H_4(CO_2.C_6H_5)_2$, from phenol and succinyl chloride, forms shining leaflets, melts at 118°, and boils at 330°.

Phenyl-allophanic Ester,  $CO{<}\begin{matrix}NH_2\\NH.CO_2.C_6H_5\end{matrix}$ (p. 393), is produced by conducting cyanic acid vapors into anhydrous phenol. A crystalline mass, decomposing at 150° into phenol and cyanuric acid.

Phenyl-ortho-formic-ester, $CH(O.C_6H_5)_3$, is formed by boiling phenol with sodium hydroxide and chloroform (as a by-product in the formation of oxybenzaldehyde). It crystallizes in white needles, melts at 71° and distils at 265°, under 50 mm. pressure. See *Berichte*, 18, 1679, for the phenol silicates.

PHENOL ALCOHOLIC ETHERS (p. 668).

Methyl Phenyl Ether, $C_6H_5.O.CH_3$, **Anisol**, is produced by heating phenol with potassium and methyl iodide or potassium methyl sulphate in alcoholic solution; by distilling anisic or methyl salicylic acid with lime or baryta (p. 668); or by leading methyl chloride into sodium phenoxide at 200° (*Berichte*, 16, 2513).

It is an ethereal-smelling liquid, boiling at 152°; its specific gravity at 15° is 0.991. Heated to 130° with hydriodic acid it decomposes into phenol and methyl alcohol. It is not reduced by zinc dust.

Bromine converts it into substitution products: *bromanisol*, $C_6H_4Br.O.CH_3$, boils at 223°; *dibromanisol* crystallizes in rhombic plates, melts at 59° and boils at 272°; *tribromanisol* melts at 87° and sublimes. Further action of bromine produces bromanil, $C_6Br_4O_2$.

Nitric acid converts anisol into two *mono-nitroanisols* (1, 4) and (1, 2).

Ethyl Phenyl Ether, $(C_6H_5).O\,C_2H_5$, **Phenetol,** is obtained from phenol and ethyl salicylic acid. It is an aromatic-smelling ether, boiling at 172°. The isoamyl ether boils at 225°.

Ethylene Phenyl Ether, $(C_6H_5.O)_2.C_2H_4$, is formed from ethylene bromide and potassium phenylate. It consists of leaflets, melting at 95°.

Phenyl Ether, $(C_6H_5)_2O$, **Phenyl Oxide,** is produced by distilling copper benzoate (together with benzoic phenyl ether) and digesting diazobenzene sulphate with phenol; also by heating phenol with zinc chloride to 350°, or better, with aluminium chloride (*Berichte*, 14, 189). It crystallizes in long needles, possesses an odor resembling that of geraniums; melts at 28°, and boils at 252°. It dissolves readily in alcohol and ether. It is not reduced on heating with zinc dust or hydriodic acid.

Thiophenol, $C_6H_5.SH$, phenyl mercaptan, is obtained by letting phosphorus pentasulphide act on phenol or sodium benzene sulphonate; or by the action of zinc and sulphuric acid upon $C_6H_5.SO_2Cl$ (p. 660). It is most readily prepared by distilling sodium benzene-sulphonate with potassium sulphydrate (*Berichte*, 17, 2080). It is a mobile, ill-smelling liquid, boiling at 168°; its specific gravity at 14° is 1.078. It dissolves readily in alcohol and ether. Like the mercaptans, it reacts readily with metallic oxides. The mercury compound, $(C_6H_5.S)_2Hg$, crystallizes from alcohol in shining needles. Silver, mercury and lead salts precipitate the alcoholic solution of thiophenol.

Phenyl mercaptan combines with α-, β- and γ-ketonic acids, yielding derivatives resembling mercaptol (p. 306 and *Berichte*, 19, 1787). Esters of phenyl thioformic acid, $C_6H_5.S.CO_2R$ (*Berichte*, 19, 1228) result from the action of thiophenyl-zinc and chlorcarbonic esters.

Phenyl Dithiocarbonic Esters, $C_6H_5.S.CS.OR$, are produced when benzene diazo-chlorides act upon xanthic esters. They decompose at 200° into COS and thiophenols (*Berichte*, 21, Ref. 915).

Phenyl Sulphide $(C_6H_5)_2S$, Benzene sulphide, is formed by distilling phenol with P_2S_5 (along with thiophenol), and in the dry distillation of sodium benzene sulphonate, as well as in the action of benzene-diazochloride upon sodium thiophenate (*Berichte*, 23, 2471). A colorless liquid, with an odor resembling that of leeks; boils at 292°, and has a specific gravity of 1.12. Nitric acid converts it into phenylsulphone.

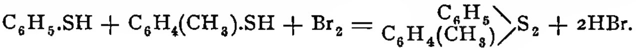
Phenyl Disulphide $(C_6H_5)_2S_2$, results from the oxidation of thiophenol with dilute nitric acid, and by the action of iodine upon aqueous potassium thiophenate:

$$2C_6H_5.SK + I_2 = (C_6H_5)_2S_2 + 2KI;$$

also, when an alcoholic solution of benzene sulpho-chloride is reduced with potassium cyanide.

It crystallizes from alcohol in shining needles, melting at 60°. Nitric acid oxidizes it to benzene sulphonic acid, and nascent hydrogen converts it into thiophenol. The same occurs by the use of K_2S (*Berichte*, 19, 3129).

Phenyl-disulphides, containing two *different* radicals, result from the action of bromine upon a mixture of two thiophenols (*Berichte*, 19, 3132; 20, 189):—



$$C_6H_5.SH + C_6H_4(CH_3).SH + Br_2 = \begin{matrix} C_6H_5 \diagdown \\ C_6H_4(CH_3) \diagup \end{matrix} S_2 + 2HBr.$$

PHENOL SUBSTITUTION PRODUCTS.

The introduction of halogen atoms considerably increases the acid character of phenol; thus, trichlorphenol readily decomposes the alkaline carbonates. When fused with potassium hydroxide the halogen is replaced by the hydroxyl group (p. 667):

$$C_6H_4Cl.OH + KOH = C_6H_4(OH)_2 + KCl.$$

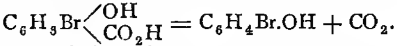
In this reaction it frequently occurs that not the corresponding isomerides, but rather, the more stable derivative results; for example, all the bromphenols yield resorcinol.

Chlorine and bromine react readily; this is exemplified in bromine precipitating tribromphenol directly upon its introduction into phenol solutions. The iodo-derivatives are formed by adding iodine and iodic acid to a dilute potassium hydroxide solution of phenol:—

$$5C_6H_6O + 2I_2 + IO_3H = 5C_6H_5IO + 3H_2O,$$

or by the action of iodine and mercuric oxide (p. 91). Di-iodophenol is the chief product in the latter case.

Substituted phenols are obtained indirectly: 1, from substituted anilines by the replacement of NH_2 by OH, which may be brought about through the diazo-compounds; 2, from the nitrophenols by replacing the nitro-group with halogens (effected through the amido- and diazo-derivatives); 3, by distilling substituted oxyacids with lime or baryta:—



$$C_6H_3Br\left\langle\begin{matrix}OH\\CO_2H\end{matrix}\right. = C_6H_4Br.OH + CO_2.$$

Bromsalicylic Acid.

Sodium amalgam causes the replacement of the halogen atoms by hydrogen.

Chlorphenols, $C_6H_4Cl.OH$. The para- and ortho-derivatives are produced by leading chlorine into boiling phenol; they can be separated by fractional distillation. The three chlor-compounds may be obtained perfectly pure from the corresponding chlor-anilines (from the chlor-nitro-benzenes). (1, 2)-*Chlorphenol* (also produced from volatile ortho-nitro-phenol) boils at 176°, solidifies at —12°, and melts at +7°. It yields pyrocatechin when fused with KOH. (1, 3)-*Chlorphenol*, from (1, 3)-chlor-aniline, melts at 28.5°, and boils at 212°. (1, 4)-*Chlorphenol* (para) consists of colorless prisms, which acquire a red color on exposure to the air, melt at 37° (41°) and boil at 217°. Hydroquinone is produced when it is fused with caustic potash. The three chlorphenols have a very penetrating, adhering odor.

Dichlorphenol, $C_6H_3Cl_2.OH$, from phenol (1, 2, 4 — OH in 1), melts at 43° and boils at 210°. It yields (1, 2, 4)-trichlorbenzene with PCl_5. **Trichlorphenol**, $C_6H_2Cl_3.OH$ (1, 3, 5, OH) (compare p. 589), obtained by acting on phenol with chlorine, melts at 68°, boils at 244°, and reacts acid. **Pentachlorphenol**, $C_6Cl_5.OH$, formed by the chlorination of phenol in presence of $SbCl_3$, melts at 187°.

Bromphenols, $C_6H_4Br.OH$ (*Annalen*, 234, 129). On conducting bromine vapors into phenol, or in brominating the glacial acetic acid solution of phenol we obtain chiefly (1, 4)- and (1, 2)-monobromphenol; under certain conditions it appears that (1, 3) is also produced. They are obtained pure from the bromanilines.

(1, 2)-*Bromphenol*, from (1, 2)-bromaniline and from (1, 2)-nitrophenol, is a liquid, boiling at 195°. (1, 3)-*Bromphenol*, from (1, 3)-bromaniline, melts at 32–33°, and boils at 236°. (1, 4)-*Bromphenol* is formed in largest quantity when phenol is treated with bromine, and has also been obtained from (1, 4)-bromaniline and from bromsalicylic acid. It consists of large crystals, melting at 66° (66.4°) and boiling at 238°. PBr_5 converts it into (1, 4)-dibrombenzene.

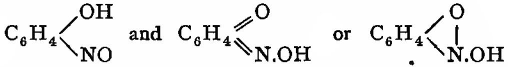
Dibromphenol, $C_6H_3Br_2.OH$ (1, 2, 4 — OH in 1), from phenol, melts at 40°. **Tribromphenol**, $C_6H_2Br_3(OH)$ (1, 3, 5, OH), is directly precipitated from aqueous phenol solutions by bromine water. It crystallizes from alcohol in silky needles, melting at 92°. PBr_5 converts it into tetrabrombenzene, melting at 98°. Nitric acid converts it into picric acid. **Tetrabromphenol**, C_6HBr_4OH, melts at 120°; **Pentabromphenol**, C_6Br_5OH, at 225°.

Iodophenols, $C_6H_4I.OH$. When phenol is acted upon by iodine and iodic acid three mono-iodo-phenols are said to be formed; of these the ortho- and meta- volatilize with steam, the para- does not (*Berichte*, 6, 1251).

(1, 2)-*Iodophenol* is obtained from (1, 2)-amido-phenol and from iodosalicylic acid. It is also produced when iodine acts upon sodium phenoxide (*Berichte*, 16, 1897). It melts at 43° and when fused with KOH yields pyrocatechin (at 200°) and resorcinol. (1, 4)-*Iodophenol*, from phenol, (1, 4)-amidophenol and (1, 4)-iodo-aniline, melts at 89°, and when fused with KOH forms hydroquinone at 160°, but resorcinol at higher temperatures.

NITROSO-DERIVATIVES OF PHENOL.

The nitrosophenols, analogous to the nitroso-benzenes (p. 591), were first made by the action of nitrous acid upon phenols, and again they are obtained from the quinones by the action of hydroxylamine, and may, therefore, be considered as isonitroso-derivatives (p. 191), or quinoximes (see quinone). In accordance with their mode of formation they have the formulas of nitrosophenols or of quinoximes (Goldschmidt, *Berichte*, 7, 213, 801):—



$$C_6H_4\Big\langle\begin{matrix}OH\\NO\end{matrix} \quad \text{and} \quad C_6H_4\Big\langle\begin{matrix}O\\N.OH\end{matrix} \quad \text{or} \quad C_6H_4\Big\langle\begin{matrix}O\\|\\N.OH\end{matrix}$$

Nitrosophenol. Quinoxime.

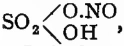
These formulas are probably tautomeric. The formation of quinone-dioxime argues in favor of the formula ascribed to quinoxime (p. 675); it is also supported by the deportment of the two nitrosonaphthols with hydroxylamine, and their ethers when reduced (see nitrosonaphthols, *Berichte*, 18, 571); further, by the action of methyl hydroxylamine upon naphthoquinones (*Berichte*, 18, 2224), by the feeble basic character of the nitrosophenols (*Berichte*, 18, 3198), and the formation of hypochlorous esters, $C_6H_4(O).NOCl$, when acted upon by bleaching lime (*Berichte*, 19, 280). An argument in favor of the nitrosophenol formula is found in their oxidation to nitrophenols, and subsequent reduction to amidophenols.

The so-called nitrosophenols are formed :—

1. By the action of nitrous acid upon the phenols :—

$$C_6H_5.OH + NO_2H = C_6H_4(NO).OH + H_2O.$$

Phenol is dissolved in a dilute alkaline hydroxide, the equivalent amount of potassium nitrite added, the solution cooled with ice, and gradually supersaturated with dilute sulphuric or acetic acid (*Berichte*, 8, 614).

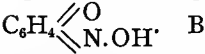
Instead of nitrous acid we may employ the action of nitro-sulphuric acid,  $SO_2\begin{cases}O.NO\\OH\end{cases}$, upon aqueous phenols (*Annalen*, 188, 353).

In both reactions nitrous acid is liberated and occasions the production of considerable resin. Hence, it is advisable to employ the nitrites of heavy metals, which are decomposed by the phenols themselves (*Berichte*, 16, 3080).

In many cases the action of amyl nitrite upon sodium phenoxides is adapted for this purpose.

It is noteworthy that while the mono-hydric phenols yield only mono-nitroso-compounds, two nitroso-groups directly enter the divalent phenols of the meta-series (like resorcinol and orcinol).

2. By the action of HCl-hydroxylamine upon quinones in aqueous or alcoholic solution. Free hydroxylamine reduces the quinones to hydroquinones (*Berichte*, 17, 2061).

p-Nitrosophenol, Quinoxime, $C_6H_4(NO).OH$, or  $C_6H_4\begin{cases}O\\N.OH\end{cases}$. Besides the general methods just mentioned, it is also obtained by a peculiar decomposition of nitroso-dimethyl- or diethyl aniline (p. 602) with sodium hydroxide :—

$$C_6H_4(NO).N(CH_3)_2 + NaOH = C_6H_4(NO).ONa + NH(CH_3)_2.$$

It is produced, further, by the action of hydroxylamine hydrochloride upon an aqueous solution of quinone, $C_6H_4O_2$ (see above).

Preparation.—It is made from phenol by the action of NO_2K and acetic acid (*Berichte*, 7, 967), or nitroso-sulphuric acid (*Annalen*, 188, 360; *Berichte*, 21, 429). Its production from nitroso-dimethyl-aniline is more convenient. The pure (free from alcohol) hydrochloride of the latter is introduced into boiling, dilute sodium hydroxide, the dimethyl-amine formed is distilled off, the residue acidified with dilute sulphuric acid, and then shaken with ether (*Berichte*, 7, 964, and 8, 622). We can easily obtain sodium nitrosophenylate by adding phenol (1 molecule), and then amyl nitrite (1 molecule) to a concentrated solution of sodium ethylate (1 molecule), and allowing the whole to evaporate over sulphuric acid (*Berichte*, 17, 400). The free nitrosophenol is obtained by decomposing the sodium salt with dilute sulphuric acid (*Berichte*, 17, 803).

Pure nitrosophenol crystallizes from hot water in colorless, delicate needles, which readily brown on exposure, and from ether it separates in large, greenish-brown leaflets. It is soluble in water, alcohol and ether, and imparts to them a bright green color. When heated it melts with decomposition, and deflagrates at 110–120°. The *sodium salt* crystallizes in red needles, containing two molecules of water; salts of the heavy metals throw out dark, amorphous precipitates.

Nitric acid and potassium ferricyanide in alkaline solution, oxidize *p*-nitrosophenol to *p*-nitrophenol. Tin and hydrochloric acid reduce it to *p* amidophenol. Hydrochloric acid converts it into dichloramido-phenol. With nitrous acid and with hydroxylamine, it yields diazo-phenol:—

$$C_6H_4(OH)NO + NH_2.OH = C_6H_4(OH).N_2.OH + H_2O.$$

In a similar manner it forms azo-compounds with the amines (p. 641); these are obtained, too, on fusion with caustic alkali. On adding a little concentrated sulphuric acid to a mixture of nitrosophenol and phenol, we obtain a dark red coloration, which changes to dark blue upon adding caustic potash (p. 668).

Other phenols, like naphthol, resorcinol and orcinol, yield similar nitroso-derivatives. These same products can also be prepared from the corresponding quinones, by the action of hydroxylamine hydrochloride (*Berichte*, 17, 2060).

When hydroxylamine hydrochloride acts upon *p*-nitrophenol (or upon quinone or hydroquinone in hydrochloric acid solution) we get *Quinone Dioxime*, $HO.N:C_6H_4:N.OH$ (*Berichte*, 20, 613), crystallizing from hot water in yellow needles. It is not as acid as nitrosophenol, and decomposes on heating to 240°. Stannous chloride and hydrochloric acid reduce it to *p*-phenylene diamine, and by ferricyanide of potassium it is oxidized in alkaline solution to *p*-dinitrosobenzene (p. 591). The formation of quinone-dioxime confirms the assumption of nitrosophenol being a mono-oxime of quinone (p. 674).

NITRO-PRODUCTS OF PHENOL.

The phenols, like the anilines, are very readily nitrated. The entrance of the nitro-groups increases their acid character very considerably. All nitrophenols decompose alkaline carbonates. Trinitrophenol is a perfect acid in its behavior; its chloranhydride, $C_6H_2(NO_2)_3Cl$, reacts quite readily with water, re-forming trinitrophenol (p. 667). The benzene nucleus of the nitrophenols is capable of ready substitution with the halogens; whereas the nitrohydrocarbons are chlorinated with difficulty.

Dilute nitric acid converts phenol into ortho- and para-mononitrophenol (in the cold it is chiefly the para-compound which is formed).

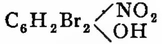
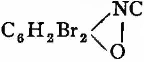
Preparation.—Gradually add one part phenol to a cooled solution of two parts of nitric acid (specific gravity 1.34) in four parts of water. The oil which separates is washed with water and distilled with steam, when the volatile (1, 2)-nitrophenol distils over, while the non-volatile (1, 4)-nitrophenol remains. It is extracted from the residue by boiling with water.

o- and *p*-Nitrophenols are obtained by heating the corresponding chlor- and brom-nitrobenzenes with caustic potash to 120°, whereas *m*-nitrobenzene does not react under similar circumstances (p. 588). Ortho- and para-nitrophenols are likewise produced from the corresponding nitranilines by heating with alkalies (p. 598). *m*-Nitrophenol is formed from *m*-nitraniline (from ordinary dinitrobenzene) by boiling the diazo-compound with water. See *Berichte*, 19, 2979, for the benzoyl derivatives of the nitrophenols.

Mononitrophenols, $C_6H_4OH(NO_2)$. The volatile *orthonitrophenol* (1, 2) crystallizes in large yellow prisms, is but slightly soluble in water, and readily volatilizes with steam. It has a peculiar odor, and sweetish taste; melts at 45°, and boils at 214°. (1, 2)-Chlornitro-benzene is obtained from it by PCl_5. Its sodium salt is anhydrous, and forms dark red prisms. The *methyl ether*, $C_6H_4(NO_2).O.CH_3$, melts at + 9°, and boils at 265°. Caustic potash does not decompose it.

(1, 3)-*Nitrophenol*, from (1, 3)-nitraniline, is rather readily soluble in cold water, forms yellow crystals, melts at 96°, and is not volatilized with steam. Its *methyl ether* melts at 38° and boils at 254°.

(1, 4)-*Nitrophenol* crystallizes from hot water in long, colorless needles, which become red on exposure. It is colorless and melts at 114°. PCl_5 converts it into (1, 4)-chlornitrobenzene. The potassium salt crystallizes in yellow needles with two molecules of water. The *methyl ether* melts at 48°, and boils at 260°; it forms (1, 4)-nitraniline when heated with ammonia. Nitrophenol can, on the one hand, be changed to quinone, on the other, into anisic acid.

Bromine converts *p*-nitrophenol into dibrom-*p*-nitrophenol,  $C_6H_2Br_2\begin{cases}NO_2\\OH\end{cases}$ (1, 2, 4, 6, OH in 1), melting at 141°. This yields Dibrom-*p*-amido-phenol, when reduced with tin and hydrochloric acid. The latter (its $SnCl_4$-salt) is converted by bleaching lime into dibrom-quinone-chlorimide,  $C_6H_2Br_2\begin{cases}NCl\\ \mid\\O\end{cases}$, which yields indophenol dyestuffs (see quinone chlorimides) with phenols.

α-**Dinitrophenol,** $C_6H_3(NO_2)_2.OH$ (1, 2, 4—OH in 1), is formed by the direct nitration of phenol, as well as of (1, 2)- and (1, 4)-nitrophenol; by boiling *α*-dinitro-chlor- and dinitro-brom-benzene (p. 589) with alkalies, and (together with *β*-dinitrophenol) by oxidizing metadinitrobenzene with alkaline potassium ferricyanide. It crystallizes from alcohol in yellow plates, and melts at 114°. PCl_5 changes it to dinitrochlorbenzene. Its *methyl ether* melts at 86°, and is saponified by boiling alkalies. The ether is transformed into *α*-dinitraniline by heating with ammonia. From this (1, 3)-dinitrobenzene may be prepared by replacing the amido group by hydrogen (through the diazo-compound).

β-**Dinitrophenol** (1, 2, 6—OH in 1) is produced with the former in the nitration of (1, 2)-nitrophenol. It yields needles, melting at 64°. By replacing its OH-group with hydrogen it passes into (1, 3)-dinitrobenzene.

Further nitration converts both dinitrophenols into picric acid. Three isomeric dinitrophenols are obtained by the nitration of (1, 3)-nitrophenol; these melt at 104°, 134° and 141°. Further action of nitric acid converts them into trinitroresorcinol.

Trinitrophenols, $C_6H_2(NO_2)_3.OH$. **Picric Acid** is obtained by the nitration of phenol, of (1, 2)- and (1, 4)-nitrophenol, and of the two dinitrophenols; also, by the oxidation of symmetrical trinitrobenzene with potassium ferricyanide. Its structure is therefore 1, 2, 4, 6 (OH in 1) (p. 589).

Picric acid is produced in the action of concentrated nitric acid upon various organic substances, like indigo, aniline, resins, silk, leather and wool.

Preparation.—Add phenol (1 part) very gradually to concentrated nitric acid, slightly warmed. The reaction proceeds with much energy, and disengages brown vapors. Next add three parts fuming nitric acid and boil for some time, until the evolution of vapors ceases. The resulting resinous mass is boiled with hot water. To purify the picric acid obtained, convert the latter into its sodium salt, and to its solution add sodium carbonate when sodium picrate will separate in a crystalline form.

Picric acid crystallizes from hot water and alcohol in yellow leaflets or prisms which possess a very bitter taste. It dissolves in 160 parts of cold water and rather readily in hot water. Its solution imparts a beautiful yellow color to silk and wool. It melts at 122.5°, and sublimes undecomposed when carefully heated. The *potassium salt*, $C_6H_2(NO_2)_3OK$, crystallizes in yellow needles, which dissolve in 260 parts of water at 15°. The *sodium salt* is soluble in 10 parts water at 15°, and is separated from its solution by sodium carbonate. The *ammonium salt* consists of beautiful, large needles, and is applied in explosive mixtures. All the picrates explode very violently when heated or struck.

Phosphorus pentachloride converts picric acid into trinitro-chlorbenzene, $C_6H_2(NO_2)_3Cl$ (p. 590), which reverts to picric acid on boiling with water.

The *methyl ester* of picric acid is also produced in the nitration of anisol (p. 671) and crystallizes in plates, melting at 65°, and subliming. Alcoholic potash saponifies it. The *ethyl ester* consists of colorless needles, which brown on exposure, and melt at 78.5°.

Picric acid forms beautiful crystalline derivatives with many benzene hydrocarbons, *e.g.*, benzene, naphthalene and anthracene. The *benzene derivative*, $C_6H_2(NO_2)_3OH.C_6H_6$, crystallizes in needles, melting at 85–90°. In dry air or with hot water it decomposes into its components.

The so-called isopicric acid, obtained by the energetic nitration of (1, 3)-nitrophenol, is trinitroresorcinol, $C_6H(NO_2)_3.(OH)_2$(styphnic acid).

Picric acid is converted by potassium cyanide into the potassium salt of *isopurpuric* or *picrocyaminic acid*, $C_8H_5N_5O_6$, which is not stable in a free state. To obtain the salt the hot solution of 1 part picric acid in 9 parts of water is poured gradually into a solution of two parts of potassium cyanide in four parts of water, at a temperature of 60°. The liquid assumes a dark red color, and when it cools a crystalline mass separates, which is washed with cold water and recrystallized from hot water.

The *potassium salt*, $C_8H_4N_5O_6K$, crystallizes in brown leaflets with green-gold lustre, and serves as a substitute for *archil*. It dissolves in hot water and alcohol with a purple red color. It explodes at 215°. The other salts of isopurpuric acid are obtained by double decomposition.

The dinitrophenols yield similar derivatives with potassium cyanide.

Two isomeric **Trinitrophenols** (β- and γ-) are obtained by nitrating the dinitrophenols prepared from meta-nitrophenol and are very similar to picric acid. β-Trinitrophenol melts at 96°; γ-trinitrophenol at 117° (*Berichte*, 16, 235).

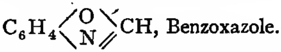
Innumerable chlornitrophenols have been obtained by the action of the halogens upon the nitrophenols, or by nitration of the halogen derivatives.

AMIDO-DERIVATIVES OF PHENOL.

These, like the anilines, are obtained by the reduction of the nitrophenols. In the case of the poly-nitrated phenols, ammonium sulphide occasions but a partial, tin and hydrochloric acid, however, a complete reduction of the nitro-group (p. 592). Thus, dinitrophenol, $C_6H_3(NO_2)_2.OH$, yields nitro-amido-phenol, $C_6H_3.(NO_2)(NH)_2.OH$, and diamido-phenol, $C_6H_3(NH_2)_2.OH$.

The amido-group considerably diminishes the acid character of the phenols. This class of derivatives no longer forms salts with alkalies, and only yields such compounds with the acids. Their amido-hydrogen, like that of the anilines, is replaced by acid radicals on heating with acid chlorides or anhydrides.

1. *o*-**Amidophenol**, $C_6H_4(NH_2).OH$, is produced from orthonitrophenol by reduction with tin and hydrochloric acid, and is precipitated from its HCl-salt by alkaline carbonates in colorless leaflets, which rapidly turn brown. It is more easily obtained by dissolving orthonitrophenol in alcoholic ammonia, and leading H_2S into the solution, when the phenol separates in crystalline form. It melts at 170° and is slightly soluble in water (in 50 parts). When potassium cyanate acts upon the hydrochloride of orthoamidophenol, it produces oxyphenyl urea, $C_6H_4(OH).NH.CO.NH_2$, melting at 154°. Potassium sulphocyanide forms oxyphenyl thiourea, $C_6H_4(OH).NH.CS.NH_2$, melting at 161°. *o*-Amidophenol can form *anhydro-* or *ethenyl-bases;* this it does by uniting its two side-chains to a carbon atom. These new derivatives contain both the benzene ring and that of oxazole (p. 555). As they have two carbon atoms in common, they are called *benzoxazoles:*—



$$C_6H_4\left\langle\begin{matrix}O\\N\end{matrix}\right\rangle CH,\ \text{Benzoxazole.}$$

The method pursued in producing this new class of compounds consists in heating *o*-amidophenols with acids or anhydrides. Acidyl derivatives are first formed, but they part with water:—

$$C_6H_4\left\langle\begin{matrix}OH\\NH.CHO\end{matrix}\right. = C_6H_4\left\langle\begin{matrix}O\\N\end{matrix}\right\rangle CH + H_2O.$$

Formyl Amido-phenol. Methenyl-amido-phenol.

In like manner ethenylamido-phenol is derived from acetyl amido-phenol. Phosgene, $COCl_2$, gives rise to the oxy-methenyl derivative (see below).

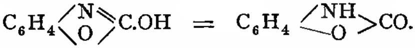
The thiohydrides of the anhydro-bases are formed:—

(1) By heating *o*-amidophenols with carbon disulphide.
(2) From *o*-oxyazobenzene by a similar treatment; as well as from the hydrazones of ortho-quinones (*Berichte*, 22, 3232, 3241).

The benzoxazoles are feeble bases. Their combinations with salts are unstable. Boiling hydrochloric acid separates them into their components.

Methenyl Amidophenol, benzoxazole, is produced by boiling *o*-amidophenol with formic acid. It consists of vitreous crystals, melting at 30.5°, and boiling at 182°.

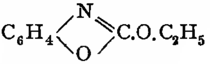
Oxymethenyl-amidophenol, or Carbonyl-Amidophenol, derived from the preceding, possesses an atomic grouping analogous to that of the lactams or lactimes (see these):—



$$C_6H_4\left<\begin{matrix}N\\O\end{matrix}\right>C.OH = C_6H_4\left<\begin{matrix}NH\\O\end{matrix}\right>CO.$$

These two formulas are probably tautomeric. The above compound is formed by allowing chlor-carbonic ester to act upon *o*-amidophenol, and by heating oxyphenyl urea (see above). NH_3 splits off. It sublimes in leaflets with mother-of-pearl lustre; these melt at 137° and yield an acetyl derivative, melting at 95° (*Berichte*, 16, 1829). It is most readily made by conducting $COCl_2$ into the benzene solution of *o*-amidophenol (*Berichte*, 20, 177). In most reactions it conducts itself as a lactam (*ibid.*); it also unites, as a CO-compound, with phenylhydrazine (*Berichte*, 19, 2270).

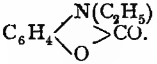
Two different ethers are obtained by replacing its hydrogen by alkyls:—



$$C_6H_4\left<\begin{matrix}N\\O\end{matrix}\right>C.O.C_2H_5$$

Lactime Ether.

and



$$C_6H_4\left<\begin{matrix}N(C_2H_5)\\O\end{matrix}\right>CO.$$

Lactam Ether.

The *lactime ether* is produced by acting upon *o*-amidophenol hydrochloride with imido-carbonic ester (*Berichte*, 19, 2655). It is an oil with peculiar odor, and boils at 225–230°. When digested with concentrated hydrochloric acid, it breaks down into ethyl chloride and oxymethenyl-amido-phenol.

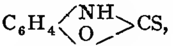
The *lactam ether* is formed when ethyl iodide and carbonyl-amidophenol interact in alkaline solution (*Berichte*, 19, 2268; 20, 177). It melts at 29°, and when heated with concentrated hydrochloric acid to 180°, it is resolved into carbon dioxide and ethyl-amido-phenol.

The *sulphur* compound, corresponding to oxymethenyl-amidophenol,

$$C_6H_5\left<\begin{matrix}N\\O\end{matrix}\right>C.SH$$

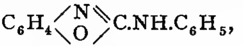
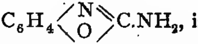
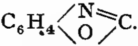
Thiohydryl-methenyl-amido-phenol.

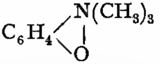
or



$$C_6H_4\left<\begin{matrix}NH\\O\end{matrix}\right>CS,$$

Thiocarbonyl-amido-phenol.

is produced either by the action of carbon disulphide upon *o*-amidophenol, or of potassium xanthate upon the hydrochloride; further, upon heating oxyphenyl sulphurea (see above) (*Berichte*, 16, 1825; 20, 178). It melts at 193–196°, and dissolves in alkalies and ammonia. When boiled with aniline it becomes **Anilido-carbamido-phenol,**  $C_6H_4\left<\begin{matrix}N\\O\end{matrix}\right>C.NH.C_6H_5$, melting at 173°. **Amido-carbamido-phenol,**  $C_6H_4\left<\begin{matrix}N\\O\end{matrix}\right>C.NH_2$, isomeric with *phenylene urea* (*Berichte*, 23, 1047), is formed on boiling oxyphenyl thiourea (p. 679) with mercuric oxide. It crystallizes from water in large plates, melting at 130°. The ethenyl compound is a liquid, and boils at 182°. **Benzenyl-amido-phenol,**  $C_6H_4\left\langle\begin{matrix}N\\O\end{matrix}\right\rangle C.C_6H_5$, is produced by the reduction of benzoyl-ortho-nitrophenol, and when digested with hydrochloric acid yields **Benzoyl-amido-phenol,** $C_6H_4(OH).NH.CO.C_6H_5$.

Methyl iodide (3 molecules) and potassium hydroxide change *o*-amidophenol (analogous to the formation of betaïne from glycocoll, p. 316) into **Trimethyl-ammonium-phenol,**  $C_6H_4\left\langle\begin{matrix}N(CH_3)_3\\ |\\ O\end{matrix}\right.$ (*Berichte,* 13, 246), which crystallizes from water in white prisms, containing $1H_2O$. It tastes bitter, and dissolves easily in water but not in ether. It breaks up by distillation into CH_3Cl and **Dimethyl-amido-phenol,** $C_6H_4(OH).N(CH_3)_2$, which melts at 45°. Its HCl-salt,  $C_6H_4\left\langle\begin{matrix}N(CH_3)_3Cl\\OH\end{matrix}\right.$, gives the base again with silver oxide.

2. *m*-**Amidophenol,** $C_6H_4(NH_2).OH$ (1, 3), is obtained by the reduction of meta-nitrophenol with tin and hydrochloric acid. Technically, it is produced by heating resorcin to 200° with hydrochloric acid and ammonia (*Berichte,* 22, Ref. 849). In this way the alkylamines yield the alkyl-*m*-amido-phenols. The latter can also be obtained from the dialkyl-aniline sulphonic acids (*Berichte,* 22, 622). *Free-m-*amidophenol is not very stable. Nitric acid converts it into resorcin. *Dimethyl m-amidophenol* melts at 87°; *diethyl-m-amidophenol* boils at 280°. *m*-Amidophenol and its alkyl derivatives are employed in the preparation of *rhodamine dyes.*

3. *p-Amidophenol,* $C_6H_4(NH_2).OH$, is obtained by reducing *p*-nitrophenol with tin and hydrochloric acid, and by distilling amidosalicylic acid. It sublimes in shining leaflets, and melts at 184° with decomposition. It is oxidized to quinone by chromic acid, or by PbO_2 and sulphuric acid. Bleaching lime converts it, as well as its substitution products, into quinone chlorimides.

p-Amidophenetol, $C_6H_4(NH_2).O.C_2H_5$, Phenetidine, is the ethyl ether. It boils at 242°. Boiling glacial acetic acid converts it into  $C_6H_4\left\langle\begin{matrix}NH.CO.CH_3\\O.C_2H_5\end{matrix}\right.$, *phenacetin,* which has been applied as an antipyretic.

Amido-thiophenol, $C_6H_4(NH_2)SH$, (1, 2), is obtained from ortho-nitro-benzene-sulphonic chloride, $C_6H_4(NO_2).SO_2Cl$, by reduction with tin and hydrochloric acid; also from acetanilide, $C_6H_5.NH.CO.CH_3$, by heating with sulphur and fusing with caustic alkali (*Berichte,* 13, 1226). A better method to pursue is to fuse benzenyl-amidothiophenol with caustic potash (*Berichte,* 20, 2259). It crystallizes in needles; melting at 26°, and boiling at 234°.

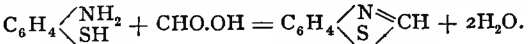
o-Amido-thiophenol (like *o*-amidophenol, p. 679) forms *thioanhydro*-compounds by linking its two side-chains to a carbon atom. Because these derivatives contain the thiazole-ring they are called *Benzothiazoles*:—

$$C_6H_4\left\langle\begin{matrix}N\\S\end{matrix}\right\rangle C.X$$

Benzothiazole.

They bear the same relation to quinoline that thiophene bears to benzene (they contain an S-atom instead of the group HC : CH, hence they show similarity to the quinoline compounds (*Berichte,* 21, 2629). They are formed:—

(1) By the action of acid chlorides or anhydrides upon the *o*-amido-thiophenols (p. 680):—

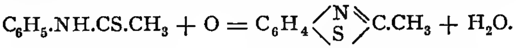


$$C_6H_4\left\langle\begin{matrix}NH_2\\SH\end{matrix}\right. + CHO.OH = C_6H_4\left\langle\begin{matrix}N\\S\end{matrix}\right\rangle CH + 2H_2O.$$

Methenyl Amido-thiophenol, Benzo-thiazole.

If acetyl chloride be used the product will be ethenyl amido-thiophenol or benzo-methyl-thiazole.

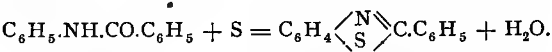
(2) By oxidizing the thioanilides with alkaline potassium ferricyanide (*Berichte*, 21, 2624; 22, 905):—



$$C_6H_5.NH.CS.CH_3 + O = C_6H_4\left\langle\begin{matrix}N\\S\end{matrix}\right\rangle C.CH_3 + H_2O.$$

Thioacetanilide. Ethenyl-amido-thiophenol.

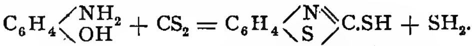
(3) By boiling the acid anilides with sulphur (in slight quantity) (*Berichte*, 13, 1223; 22, 905):—



$$C_6H_5.NH.CO.C_6H_5 + S = C_6H_4\left\langle\begin{matrix}N\\S\end{matrix}\right\rangle C.C_6H_5 + H_2O.$$

Benzanilide. Benzenyl-amido-thiophenol.

(4) The thiohydrides of the anhydrobases may be obtained from the *o*-amido-thiophenols and CS_2 (*Berichte*, 20, 1790):—



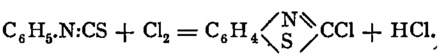
$$C_6H_4\left\langle\begin{matrix}NH_2\\OH\end{matrix}\right. + CS_2 = C_6H_4\left\langle\begin{matrix}N\\S\end{matrix}\right\rangle C.SH + SH_2.$$

Thiomethenyl-amido-thiophenol.

The benzo-thiazoles are liquids that boil without decomposition. They have an odor like that of pyridine. Their salts are not very stable. Fused alkalies decompose them into their components.

The **Methenyl-amido-thiophenol**, $C_6H_4\left\langle\begin{matrix}N\\S\end{matrix}\right\rangle CH$, benzo-thiazole (isomeric with phenyl mustard oil, $C_6H_5.N:CS$, and phenyl sulphocyanate, $C_6H_5.S.CN$), is produced on heating amidothiophenol with formic acid. It is an oil smelling like pyridine, and boiling at 230°.

Chlormethenyl-amido-thiophenol, chlorphenyl mustard-oil, C_7H_4NSCl, results from phenyl mustard-oil on heating it to 160° with PCl_5:—



$$C_6H_5.N:CS + Cl_2 = C_6H_4\left\langle\begin{matrix}N\\S\end{matrix}\right\rangle CCl + HCl.$$

It melts at 24°, and boils at 248°. It reverts to methenyl amidothiophenol by the action of tin and hydrochloric acid. The chlorine atom in it is readily adapted to double decompositions. The *hydroxide*, $C_6H_4(SN)C.OH$, oxy-phenyl mustard-oil, melts at 136°, and dissolves readily in alkalies. Sodium ethylate converts the chloride into the **ethyl oxide** (ethyl oxyphenyl mustard-oil), $C_6H_4.(SN).C.O.C_2H_5$. This results from the oxidation of phenyl-sulphurethane with potassium ferricyanide (see above). It melts at 25°, and when boiled with hydrochloric acid yields the hydroxide.

The **amide** melts at 129°. The **thiohydride**, $C_6H_4(NS)C(SH)$, results when the chloride is acted upon with alcoholic sodium sulphydrate and from *o*-amidophenol and CS_2. It melts at 179° (*Berichte*, 20, 1790).

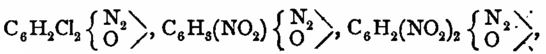
Ethenyl-amido-thiophenol, $C_6H_4\left\langle{N \atop S}\right\rangle C.CH_3$, is obtained by boiling *o*-amido-thiophenol with acetic anhydride, and by oxidizing thioacetanilide (see above). It is a liquid, boiling at 238°.

Benzenyl-amido-thiophenol, $C_6H_4\left\langle{N \atop S}\right\rangle C.C_6H_5$, results upon heating phenylbenzamide with sulphur, and also in the oxidation of thiobenzanilide with potassium ferricyanide (see above and *Berichte*, 19, 1068). It crystallizes in long needles, melting at 114°.

Dinitro-amido-phenol, $C_6H_2(NH_2).(NO_2)_2.OH$, *picramic acid*, is obtained by reducing ammonium picrate in alcoholic solution with hydrogen sulphide. It forms red needles, which melt at 165°. It yields red-colored crystalline salts with bases.

Triamidophenol, $C_6H_2(NH_2)_3.OH$, is obtained from picric acid by the action of phosphorus iodide, or by tin and hydrochloric acid (*Berichte*, 16, 2400). When set free from its salts it decomposes very quickly. Its salts, with 3 equivalents of acids, crystallize well. The HI-salt, $C_6H_3O(NH_2)_3.3HI$, crystallizes in colorless needles. These salts color water which is faintly alkaline, and even spring water, a beautiful blue. If ferric chloride be added to the solution of the hydrochloride, it will become deep blue in color, and brown-blue needles with metallic lustre will separate; they are *HCl-amido-di-imido-phenol*, $C_6H_2(OH)(NH_2)\left\langle{NH \atop NH}\right\rangle$, which dissolves in water with a beautiful blue color.

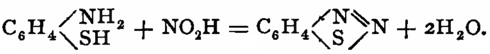
Diazo-compounds of the Phenols, such as *phenol diazochloride*, $C_6H_5\left\langle{N_2Cl \atop OH}\right.$, result from the action of nitrous acid upon the amido-phenols; free diazo-compounds have been obtained from the substituted amido-phenols, *e.g.*:—



$$C_6H_2Cl_2\left\{{N_2 \atop O}\right\rangle, \quad C_6H_3(NO_2)\left\{{N_2 \atop O}\right\rangle, \quad C_6H_2(NO_2)_2\left\{{N_2 \atop O}\right\rangle,$$

in which the second affinity of the diazo-group appears to be joined to oxygen (p. 630).

Analogous sulphur-compounds, the *diazo-sulphides*, are formed when nitrous acid acts upon the *o*-amidothiophenols and their anhydro-compounds (*Berichte*, 22, 905):—



$$C_6H_4\left\langle{NH_2 \atop SH}\right. + NO_2H = C_6H_4\left\langle{N \atop S}\right\rangle N + 2H_2O.$$

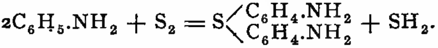
They are very stable and crystallize well. They distil without decomposition under reduced pressure.

o-Phenylene-diazosulphide, $C_6H_4\left\langle{N \atop S}\right\rangle N$, is easily produced when nitrous acid acts upon benzenyl-amidothiophenol. It forms large plates, having a pleasant odor. It melts at 37°, and volatilizes with steam.

The *azo-derivatives* of the phenols are produced by reduction of the nitrophenols in alcoholic potassium hydroxide solution (p. 641); further, by the action of the anilines upon the nitrosophenols. They are perfectly analogous to the azo-derivatives of the benzenes (*Berichte*, 17, 272).

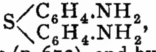
Amidothiophenyls or Thioanilines.

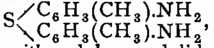
These compounds result when nitrothiophenyls are reduced. The diamidophenyl sulphides are also produced from anilines by boiling the latter with sulphur:—



$$2C_6H_5.NH_2 + S_2 = S\left\langle\begin{array}{l}C_6H_4.NH_2\\C_6H_4.NH_2\end{array}\right. + SH_2.$$

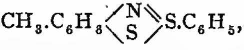
The alkyl anilines and sulphur yield derivatives resembling the thiazoles (*Berichte*, 22, 67). Sulphur chloride, or thionyl chloride, $SOCl_2$ (*Berichte*, 21, 2056; 23, 552), converts the dialkylanilines into alkylic-thio-anilines. The mono-alkyl-anilines, by like treatment, yield *Thionyl anilines*, *e. g.*, $SO\ (C_6H_4.NH.CH_3)_2$ (*Berichte*, 23, 3020). Silver nitrate and ammonia desulphurize the dialkyl-compounds, with the formation of oxydimethylanilines, *e. g.*, $O[C_6H_4.N(CH_3)_2]_2$ (*Berichte*, 21, 2056).

Diamidophenyl Sulphide,  $S\left\langle\begin{array}{l}C_6H_4.NH_2\\C_6H_4.NH_2\end{array}\right.$, *Thioaniline*, results from the reduction of dinitrophenyl-sulphide (p. 672), and by heating aniline and sulphur to 150–160°, then adding litharge (*Berichte*, 4, 384). It crystallizes from hot water in long needles, melting at 105°.

Thio-p-toluidine,  $S\left\langle\begin{array}{l}C_6H_3(CH_3).NH_2\\C_6H_3(CH_3).NH_2\end{array}\right.$, Diamidotolyl Sulphide, is obtained by heating *p*-toluidine with sulphur and litharge to 140°. It crystallizes in large leaflets, melting at 103°. The sodium salts of thio- and dithio-toluidine sulphonic acids dye unmordanted cotton (*Berichte*, 21, Ref. 877).

The bi-diazo-salts of thio-toluidine combine with naphthylamine-sulphonic acids and yield disazo dyes of a brown-red color (*Berichte*, 20, 664).

Dehydrothio toluidine, $C_{14}H_{12}N_2S$, is formed when thio-*p*-toluidine and sulphur are heated to 185° (*Berichte*, 22, 423, 581, 970). It crystallizes from alcohol in yellow needles, melting at 191°. Its alcoholic solution shows a beautiful blue fluorescence. Another base, very similar to the preceding, is formed at the same time it is produced. The sodium sulphonate of the latter is *primuline*, which dyes unmordanted cotton yellow if it be diazotized upon the fibre. It can also combine with phenols and anilines.

Benzenyl-p-m-amido-thiocresol,  $CH_3.C_6H_3\left\langle\begin{array}{c}N\\S\end{array}\right\rangle S.C_6H_5$, results when the amido-group is eliminated from dehydro-thio-toluidine. It may be synthetically prepared by oxidizing thio-benz-toluidine, $CH_3.C_6H_4.NH.CS.C_6H_5$ (p. 682) (*Berichte*, 22, 1063).

PHENOL-SULPHONIC ACIDS.

Ortho- and Para-phenolsulphonic Acid, $C_6H_4(OH).SO_3H$, are formed when phenol dissolves in concentrated sulphuric acid; at medium temperatures the former is the more abundant, but readily passes into the *para-* on the application of heat.

Preparation.—To obtain the acids, the solution of phenol in sulphuric acid (equal parts) is diluted with water and saturated with calcium carbonate. The filtrate from the gypsum, containing the calcium salts, is boiled with potassium carbonate, thus producing potassium salts. On allowing it to crystallize the potassium salt, $C_6H_4(OH).SO_3K$, of the *para*-acid first separates in hexagonal plates; later the ortho-salt, $C_6H_4(OH).SO_3K + 2H_2O$, crystallizes out in prisms, which soon effloresce on exposure (*Annalen*, 205, 64).

The free acids can be obtained in crystalline form by the slow evaporation of their aqueous solution. When the aqueous ortho-acid is boiled it changes to para. The aqueous solution of the ortho-acid is applied as an antiseptic under the name of *aseptol* (*Berichte*, 18, Ref. 506). The para-acid yields quinone if its sodium salts be oxidized with MnO_2 and sulphuric acid. PCl_5 converts it into (1, 4)-chlor-phenol and (1, 4)-dichlorbenzene. When the ortho-acid is fused with KOH at 310° it yields pyro-catechin—hence it belongs to the ortho-series; the para-acid does not react at 320°, and at higher temperatures yields diphenols.

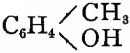
The iodation of the para-acid produces *Di-iodo-phenol sulphonic Acid*, $C_6H_2I_2.(OH).SO_3H$. This is applied as an antiseptic, bearing the name *Sozo-iodol* (*Berichte*, 21, Ref. 250).

Meta-phenolsulphonic Acid (1, 3) is produced when meta-benzene-disulphonic acid (p. 663) is heated to 170–180° with aqueous potassium hydroxide (*Berichte*, 9, 969). The potassium salt, $C_6H_4(OH).SO_3K + H_2O$, effloresces in the air; the free acid consists of delicate needles, and contains 2 molecules of H_2O. Fusion with potassium hydroxide at 250° converts it into resorcinol (1, 3). When para-benzene-disulphonic acid is heated with caustic alkali, meta-phenolsulphonic acid is also produced at first, but it yields resorcinol later.

Phenol-disulphonic Acid, $C_6H_3(OH).(SO_3H)_2$, results from the action of an excess of sulphuric acid upon phenol, also upon (1, 2)- and (1, 4)-phenolsulphonic acid, hence its structure is (1, 2, 4—OH in 1). It is further produced in the action of SO_4H_2 upon diazobenzene sulphate. The solutions of the acid and its salts are colored a dark red by ferric chloride.

Phenol-trisulphonic Acid, $C_6H_2(OH).(SO_2H)_3$ (1, 3, 5, OH), is obtained when concentrated sulphuric acid and P_2O_5 act upon phenol. It crystallizes in thick prisms with $3\frac{1}{2}H_2O$.

HOMOLOGOUS PHENOLS.



1. **Cresols**, $C_6H_4\left\langle\begin{array}{l}CH_3\\OH\end{array}\right.$, Oxy-toluenes.

The cresol contained in coal-tar appears to contain three isomerides, but they cannot be separated. They are obtained pure from the amido-toluenes (toluidines) by replacing the amido-group by hydroxyl, and from the toluene-sulphonic acids by fusion with potassium hydroxide. The cresols are changed to toluene when heated with zinc dust. Sodium and carbon dioxide produce the corresponding cresotinic acids, $C_6H_3(CH_3)(OH).CO_2H$.

Ortho-cresol (1, 2), from ortho-toluidine and ortho-toluene-sulphonic acid, melts at 31°, and boils at 188°. It is obtained from carvacrol (p. 688) when heated with P_2O_5. It yields salicylic acid (1, 2) on fusion with potassium hydroxide; Fe_2Cl_6 colors it blue. For its nitro-derivatives, see *Berichte*, 15, 1860, and 17, 270.

Nitroso-o-cresol, from *o*-cresol by means of nitrous acid and from toluquinone and hydroxylamine (p. 676), melts at 134°. Consult *Berichte*, 17, 351, for azo- and diazo-compounds of the cresols.

Meta-cresol (1, 3) is formed from thymol (p. 688), when digested with phosphoric anhydride:—

$$C_{10}H_{14}O = C_7H_7.OH + C_3H_6,$$

also from *m*-toluidine (from *m*-nitrobenzaldehyde).

Meta-cresol is a thick liquid, which solidifies when exposed to cold, melts at 4–5° (*Berichte*, 18, 3443), and boils at 201°. Its benzoyl derivative, $C_7H_7O.C_7H_5O$, melts at 38°, and boils at 300°. The *methyl ether* is an oil boiling at 176°; it is oxidized by potassium permanganate to methyl-meta-oxybenzoic acid. Meta-cresol yields meta-oxy-benzoic acid on fusion with caustic potash. The nitration of meta-cresol forms a trinitro-cresol, while the ortho- and para-derivatives only yield dinitro-derivatives (*Berichte*, 15, 1864).

Trinitro-m-cresol, $C_6H_2(NO_2)_3\left\langle\begin{matrix}CH_3\\OH\end{matrix}\right.$, melts at 106°; it is also obtained from nitrococcic acid. Consult *Berichte*, 15, 1130 and 1864, upon nitrometa-cresols.

Para-cresol (1, 4), from solid paratoluidine, and from para-toluenesulphonic acid, forms colorless needles, melting at 36°, and boiling at 198°. Its odor resembles that of phenol; it dissolves with difficulty in water. Ferric chloride imparts a blue color to the aqueous solution. It yields paraoxybenzoic acid when fused with caustic potash. The *benzoyl* compound, $C_7H_7O.C_7H_5O$, crystallizes in six-sided plates, and melts at 70°. The *ethyl ether*, $C_7H_7O.C_2H_5$, is an aromatic-smelling liquid, which boils at 188°. The *methyl ether* boils at 174°. Chromic acid oxidizes it to anisic acid, $C_6H_4(O.CH_3).CO_2H$.

Consult *Berichte*, 21, 729, upon *Nitrosocresols*.

The nitration of para-cresol produces different nitro-cresols. *Dinitro-cresol*, $C_7H_5(NO_2)_2OH$ (1, 4, 2, 6), is also obtained by the action of nitrous acid upon paratoluidine (*Berichte*, 15, 1859), and as potassium or ammonium salt represents commercial *Victoria orange* or *Gold-yellow*. It consists of yellow crystals, melting at 84°, and is not as soluble in water as picric acid. Mixed with indigo-carmine it forms *emerald green* (for liqueurs), and with aniline a *carmine surrogate*. Commercial *Saffran-surrogate* is a mixture of the potassium salts of dinitro- para- and ortho-cresols.

p-Amido-*m*-thiocresol, $C_6H_3(CH_3)\left\langle\begin{matrix}SH(3)\\NH_2(4)\end{matrix}\right.$, is produced together with *p*-amido-benzoic acid by the decomposition of dehydrothiotoluidine upon fusing it with alkalies. Nitrous acid converts it into a diazo-sulphide (p. 683) (*Berichte*, 22, 1064).

Thio-cresols, $C_6H_4\left\langle\begin{matrix}CH_3\\SH\end{matrix}\right.$, Toluene sulphydrates, are obtained by the reduction of the chlorides of the three toluene sulphonic acids with zinc and hydrochloric acid (p. 672). (1, 2)-Thiocresol melts at 15°, and boils at 188°. (1, 3)-Thiocresol is a liquid, and does not solidify at —10°. (1, 4)-Thiocresol crystallizes in large leaflets, melts at 43°, and boils at 188°.

It is singular that the cresols, and all other higher phenols, cannot be oxidized with a chromic acid mixture; *the OH-group prevents the oxidation of the alkyl group.* If, however, the phenol hydrogen be replaced by alkyls or even acid groups (in the phenol ethers and esters), the alkyl is oxidized and oxyacids (their ether acids) are produced:—

$$C_6H_4\left\langle\begin{matrix}O.CH_3\\CH_3\end{matrix}\right. \text{ yields } C_6H_4\left\langle\begin{matrix}O.CH_3\\CO_2H\end{matrix}\right. .$$

To oxidize the homologous phenols it is advisable to employ their sulphuric and phosphoric acid esters—these are easily prepared—and subject them to the action of an alkaline permanganate solution (*Berichte*, 19, 3304). This oxidizing agent destroys the free phenols completely.

The oxidation of the alkyls in the sulphonic acids of the homologous benzenes is dependent upon the position of the sulpho-group. In general, *negative atoms, or atomic groups, prevent the oxidation of the alkyls in the ortho-position by acid oxidizing agents* (pp. 584 and 591), whereas alkaline oxidizers (like MnO_4K) do the reverse, that is, first oxidize the alkyl occupying the ortho-position (*Annalen*, 220, 16).

Consult *Berichte*, 14, 687, on the deportment of cresols in the animal organism.

2. Phenols, $C_8H_9.OH$.

The six possible xylenols, $C_6H_3(CH_3)_2.OH$, have been prepared partly from the corresponding xylidines, and partly by fusing isomeric xylene-sulphonic acids with potassium hydroxide. Further fusion oxidizes them to oxytoluic and oxyphthalic acids.

Ethyl Phenols, $C_6H_4(C_2H_6).OH$. The three isomerides have been prepared from the corresponding ethyl-benzene-sulphonic acids when the latter were fused with alkalies. The *ortho*-compound is a liquid, boiling at 209–210°. The *meta* boils at 202–204°. The *para* is a solid, melts at 46°, and boils at 214° (*Berichte*, 22, 2672).

3. Phenols, $C_9H_{11}.OH$.

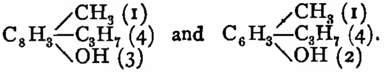
Mesitylol, $C_6H_2(CH_3)_3.OH$, from amido-mesitylene, mesitylene sulphonic acid and pseudocumidine, is crystalline, melts at 68–69°, and boils at 220°. Isomeric *Pseudocumenol*, $C_6H_2(CH_3)_3.OH$, from pseudo-cumene-sulphonic acid, consists of delicate needles, melting at 73°, and boiling at 232° (*Berichte*, 17, 2976).

p-Propyl Phenol, $C_6H_4(OH).C_3H_7$, from propyl benzenesulphonic acid, boils at 232°. *p*-Isopropyl-benzene, $C_6H_4(C_3H_7).OH$, from isopropyl-benzenesulphonic acid, melts at 61°, and boils at 229°.

4. Phenols, $C_{10}H_{13}.OH$.

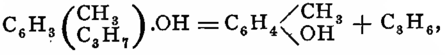
Tetramethyl Phenol, $C_6H(CH_3)_4.OH$ (1, 2, 4, 5, 6—OH in 6), *durenol*, from durene sulphonic acid, melts at 117°, and boils at 250° (*Berichte*, 18, 2843).

Methyl-propyl Phenols.—There are twenty possible isomerides. Thymol and Carvacrol merit notice. They occur in vegetable oils:—



$$C_8H_3\begin{cases}CH_3\ (1)\\ C_3H_7\ (4)\\ OH\ (3)\end{cases} \text{ and } C_6H_3\begin{cases}CH_3\ (1)\\ C_3H_7\ (4).\\ OH\ (2)\end{cases}$$

Both are derivatives of ordinary para-cymene (p. 577), and contain the normal propyl group (*Berichte*, 19, 245). In thymol the OH-group is in the meta-position with reference to the methyl group; in carvacrol, however, in the ortho-position. Both decompose into propylene and cresols when heated with P_2O_5:—



$$C_6H_3\left(\begin{matrix}CH_3\\ C_3H_7\end{matrix}\right).OH = C_6H_4\begin{cases}CH_3\\ OH\end{cases} + C_3H_6,$$

thymol yielding meta-cresol and carvacrol para-cresol.

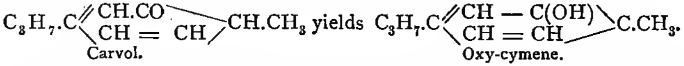
Thymol exists with cymene, $C_{10}H_{14}$, and thymene, $C_{10}H_{16}$, in oil of thyme (from *Thymus vulgaris*), and in the oils of *Ptychotis ajowan* and *Monarda punctata*. To obtain the thymol shake these oils with potassium hydroxide, and from the filtered solution precipitate thymol with hydrochloric acid. It is artificially prepared from nitrocuminaldehyde, $C_6H_3(NO_2).(C_3H_7).CHO$, by its conversion into the dichloride, reduction of the latter to cymidine, $C^6H_3.(NH_2)(C_3H_7).CH_3$, by means of zinc and hydrochloric acid, and decomposition of the diazo-compound of the latter with water (*Berichte*, 19, 245). Thymol crystallizes in large colorless plates, melting at 44° and boils at 230°. It has a thyme-like odor and answers as an antiseptic. Ordinary cymene is obtained by distilling it with P_2S_5.

Iodine and caustic potash convert thymol into *iodothymol.* This has been substituted for iodoform under the name of *annidalin.*

Nitrous acid changes thymol to *nitroso-thymol*, $C_{10}H_{12}(NO)OH$, melting at 160°. The same compound results on treating thymoquinone with hydroxylamine (p. 675 and *Berichte*, 17, 2061).

Carvacrol, $C_{10}H_{13}.OH$, *Oxycymene*, occurs already formed in the oil of certain varieties of satureja; it is produced on heating isomeric *carvol*, $C_{10}H_{14}O$, with glacial phosphoric acid (*Berichte*, 20, 12). It is artificially prepared from cymene-sulphonic acid by fusion with KOH, and by heating camphor with iodine ($\frac{1}{5}$ part) or $ZnCl_2$. It is a thick oil, solidifying at low temperatures; it melts at 0°, and boils at 236°. Distilled with P_2S_5, it yields cymene and *thiocymene*, $C_{10}H_{13}.SH$, which boils at 235°.

Carvol, $C_{10}H_{14}O$ (see above), isomeric with carvacrol, is contained in oil of cumin. It is an oil boiling at 225°. When heated with potassium hydroxide or phosphoric acid it changes to the isomeric oxycymene. In its behavior it is very much like camphor, $C_{10}H_{16}O$ (see this); it contains a CO-group, inasmuch as it combines with hydroxylamine and phenylhydrazine (*Berichte*, 17, 1578). **Carvoxime**, $C_{10}H_{14}:N.OH$, melts at 71° and is identical with nitrosohesperidine (*Berichte*, 18, 2220). According to its constitution carvol (like camphor) is a keto-derivative of a dihydrobenzene, and indeed of dihydrocymene. When it is converted into oxycymene there occurs a transposition of the reduced benzene nucleus into the normal, of the secondary ketone-form into the tertiary phenol-form (*Berichte*, 20, 491; 21, 473) (compare phloroglucin):—



$$C_3H_7.C\begin{cases}\!\!/\!\!/ CH.CO \\ \diagdown CH = CH\end{cases}\!\!\!\!\!\!>CH.CH_3 \text{ yields } C_3H_7.C\begin{cases}\!\!/\!\!/ CH - C(OH) \\ \diagdown CH = CH\end{cases}\!\!\!\!\!\!>C.CH_3.$$

Carvol. Oxy-cymene.

Isobutyl Phenol, $C_6H_4(C_4H_9).OH$, is readily obtained by heating phenol with isobutyl alcohol in the presence of $ZnCl_2$ (p. 667). It has also been prepared from isobutyl-aniline, by means of the diazo-compound. It melts at 99°, and boils at 238°.

Pentamethyl Phenol, $C_6(CH_3)_5.OH = C_{11}H_{16}O$, is obtained from amido-pentamethyl benzene (*Berichte*, 18, 1827). It melts at 125°, and boils at 267°.

DIHYDRIC PHENOLS.

$$C_6H_4\left\{\begin{matrix}OH\\OH\end{matrix}\right. \quad \left\{\begin{matrix}\text{Pyrocatechin.}\\\text{Resorcin.}\\\text{Hydroquinone.}\end{matrix}\right.$$

$$C_6H_3(CH_3)\left\{\begin{matrix}OH\\OH\end{matrix}\right. \quad \left\{\begin{matrix}\text{Orcin.}\\\text{Homo-pyrocatechin.}\end{matrix}\right.$$

$$C_6H_2(CH_3)_2\left\{\begin{matrix}OH\\OH\end{matrix}\right. \quad \left\{\begin{matrix}\text{Beta-orcin.}\\\text{Hydrophloron.}\end{matrix}\right.$$

These are obtained like the monohydric phenols, by fusing monohalogen phenols, $C_6H_4X.OH$, halogen benzenesulphonic acids and phenolsulphonic acids with potassium hydroxide (p. 666). It must, however, be observed that often the corresponding dioxy-benzenes do not result, but in their stead (especially at higher temperatures) the more stable resorcinol (1, 3). They are also produced by diazotizing the amidophenols, and by the dry distillation of aromatic dioxyacids with lime or baryta.

The dioxybenzenes belonging to the para-series, are capable of forming quinones, $C_6H_4O_2$, when oxidized.

Dioxybenzenes:—

(1) **Pyrocatechin**, $C_6H_4(OH)_2$ (1, 2), Oxyphenic Acid, Catechol, was first obtained in the distillation of catechine (the juice of *Mimosa catechu*). It is formed by the dry distillation of protocatechuic acid, $C_6H_3(OH)_2.CO_2H$, of catechuic and Moringa tannic acids, and from (1, 2)-chlor- and iodo-phenols, or (1, 2)-phenolsulphonic acid and many resins on fusion with potassium hydroxide.

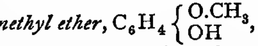
It is best prepared by heating guaiacol (from that portion of beech-wood tar boiling at 195–205°) to 200° with hydriodic acid:—

$$C_6H_4\left\langle\begin{matrix}O.CH_3\\OH\end{matrix}\right. + HI = C_6H_4\left\langle\begin{matrix}OH\\OH\end{matrix}\right. + CH_3I.$$

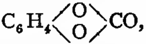
Or, ortho-phenolsulphonic acid may be fused with caustic alkalies (8 parts) to 330–360° (*Journ. pract. Chem.*, 20, 308).

Pyrocatechin crystallizes from its solutions in short, rhombic prisms, and sublimes in shining leaflets. It is soluble in water, alcohol and ether. It melts at 104°, and boils at 245°. On exposure to the air its alkaline solutions assume a green, then brown and finally a black color. Lead acetate throws out a white precipitate, $PbC_6H_4O_2$, from its aqueous solution; while lime water imparts a green color to it if concentrated. Ferric chloride colors its solution dark green, this changes to violet after the addition of a little ammonia, sodium carbonate or tartaric acid. Ferric chloride *imparts a green color to all ortho-dioxy-derivatives* in solution, even if one hydrogen atom is replaced by an alkyl. Pyrocatechin reduces cold silver solutions and alkaline copper solutions. The application of heat is required in the latter case.

Acetyl chloride produces the acetyl derivative, $C_6H_4(O.C_2H_3O)_2$, crystallizing in needles.

The *monomethyl ether*,  $C_6H_4\left\{\begin{matrix}O.CH_3\\OH\end{matrix}\right.$, **Guaiacol**, occurs in wood-tar and is produced on heating pyrocatechin with potassium hydroxide and potassium methyl sulphate to 180°. It is a colorless liquid, which boils at 200° and has a specific gravity 1.117. It dissolves with difficulty in water, readily in alcohol, ether and acetic acid. Ferric chloride gives its alcoholic solution an emerald green color. It forms crystalline salts with the alkali and alkaline earth metals. Its alkaline solutions reduce gold, silver and copper salts. Guaiacol decomposes into pyrocatechin and CH_3I (also $CH_3.OH$) when heated with hydriodic acid or fused with KOH.

The *dimethyl ether*, $C_6H_4(O.CH_3)_2$, is prepared by treating the potassium salt of the mono-methyl ether with CH_3I, and by distilling dimethyl-protocatechuic acid with lime. It is a liquid, which boils at 205°. It is identical with *veratrol*, obtained from veratric acid.

The *carbonic ester*,  $C_6H_4\langle\begin{smallmatrix}O\\O\end{smallmatrix}\rangle CO$, results from the action of chlorcarbonic ester upon pyrocatechin, and melts at 118°. Pyrogallol reacts similarly (*Berichte*, 13, 697), while, on the other hand, the mixed carbonic acid esters, *e.g.*, $C_6H_4(O.CO_2.C_2H_5)_2$ (*Berichte*, 19, 2265), are formed in the action of chlorcarbonic esters upon hydroquinone and resorcinol (as well as upon monohydric phenols).

(2) **Resorcin**, Resorcinol, $C_6H_4(OH)_2$ (1, 3), is produced from different resins (like *galbanum* and *asafœtida*) and from umbelliferon on fusion with caustic potash. It results in the same way from (1, 3)-chlor-and iodophenol, from metaphenol sulphonic acid and meta-benzene disulphonic acid, and also from various other benzene di-derivatives not included in the meta-series, *e.g.*, from the three brom-benzene sulphonic acids (p. 663) and from both benzene disulphonic acids (compare p. 689).

It was formerly obtained by distilling the extract of Brazil wood; at present, however, it is prepared technically from crude benzene disulphonic acid (*Journ. pract. Chem.*, 20, 319), and serves for the synthesis of different dyes. It is purified by sublimation and by crystallization from benzene.

Resorcin crystallizes in rhombic prisms or plates, melts at 118° when perfectly pure (otherwise at 102–110°), and boils at 276°. It dissolves readily in water, alcohol and ether, but not in chloroform and carbon disulphide. Lead acetate does not precipitate the aqueous solution (distinction from pyrocatechin). Silver nitrate is only reduced by it upon boiling; and in the cold if ammonia be present. Ferric chloride colors the aqueous solution *a dark violet.*

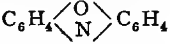
Bromine water precipitates *tribromresorcin*, $C_6HBr_3(OH)_2$, from the solution. This crystallizes from hot water in needles. By heating resorcinol with phthalic anhydride we get fluoresceïn; *the homologous metadioxybenzenes also yield fluoresceïns.* With diazo-compounds it forms azo-coloring substances (p. 643).

The *diacetyl compound*, $C_6H_4(O.C_2H_3O)_2$, is a liquid. The *diethyl ether*, $C_6H_4(O.C_2H_5)_2$, obtained by heating resorcinol with ethyl iodide and potassium hydroxide, boils at 243°, the *dimethyl ether* at 214°.

Nitrous acid, acting upon a diluted resorcinol solution (*Berichte*, 8, 633), produces dinitroso-resorcinol, $C_6H_2(OH)_2(NO)_2$ or $C_6H_2(O)_2(N.OH)_2$ (1, 3–2, 4) (p. 674), (*Berichte*, 21, 1545; 23, 3193). This crystallizes with $2H_2O$ in yellow brown leaflets, which detonate on heating to 115° C. (*Berichte*, 20, 1607). It occurs in commerce under the names *solid green*, *fast green*.

Nitric acid vapors oxidize resorcinol to *dinitroresorcin*, $C_6H_2(NO_2)_2(OH)_2$, melting at 142°. It yields dinitro-diamidobenzene when heated with ammonia. *Isodinitro-resorcin*, obtained by nitration, melts at 212°. It passes, by reduction, into *diamidoresorcin*, $C_6H_2(OH)_2.(NH_2)_2$ (1, 3–4, 6). The latter can also be easily obtained by reducing resorcin-diazobenzene with tin and hydrochloric acid (*Berichte*, 17, 881). When its ammoniacal solution is exposed to the air it oxidizes to *Diamido-resorcinol*, $C_6H_2(OH)_2(NH_2)_2$, separating in steel blue needles (*Berichte*, 22, 1653). It is soluble in caustic potash, and on application of heat yields dioxyquinone (p. 702).

When cold nitric acid acts on resorcinol and various gum-resins (galbanum, gum-ammoniac), or by nitrating metanitrophenol, we get *Trinitro-resorcinol*, $C_6H(NO_2)_3(OH)_2$ (Styphnic Acid, Oxypicric Acid) (*Berichte*, 21, 3119), which crystallizes in yellow hexagonal prisms or plates. It melts at 175°, and sublimes when carefully heated, but explodes on rapid heating. It dissolves easily in alcohol and ether, but with difficulty in water. Ferrous sulphate and lime water at first color it green, but this disappears (picric acid colors it blood-red). Trinitro-resorcinol is a strong dibasic acid, yielding well crystallized acid and neutral salts. The *diethyl ester* is solid, and melts at 120°.

If resorcinol be heated with sodium nitrite it forms a deep-blue dye, soluble in water. Acids turn this red (*Berichte*, 17, 2617). It is used as an indicator under the name of *lacmoid* (*Berichte*, 18, Ref. 126). Nitric acid, containing nitrous acid, converts resorcin into two dyes: *diazoresorcin* and *diazoresorufin* (Weselsky). These have also been called *resorufin* or *resorutamin*, $C_{12}H_7NO_3$, and *resazurin*, $C_{12}H_7NO_4$. They appear to be derivatives of phenoxazine,  $C_6H_4\langle\begin{smallmatrix}O\\N\end{smallmatrix}\rangle C_6H_4$ (Nietzki, *Berichte*, 22, 3020; 23, 718).

3. **Hydroquinone**, $C_6H_4(OH)_2$ (1, 4), was first obtained by the dry distillation of quinic acid and by digesting its aqueous solution with PbO_2:—

$$C_7H_{12}O_6 + O = C_6H_6O_2 + CO_2 + 3H_2O.$$

It results also on boiling the glucoside arbutin with dilute sulphuric acid, or by the action of emulsin:—

$$\underset{\text{Arbutin.}}{C_{12}H_{16}O_7} + H_2O = \underset{\text{Hydroquinone.}}{C_6H_6O_2} + \underset{\text{Glucose.}}{C_6H_{12}O_6}.$$

It is synthetically prepared by fusing (1, 4)-iodophenol with potassium hydroxide at 180°; or from oxysalicylic acid, and from para-amidophenol. Worthy of note is the formation of various hydroquinone derivatives from succino-succinic ester (p. 566), or that of hydroquinone in the distillation of succinates. The most convenient method of preparing it consists in reducing quinone with sulphurous acid: $C_6H_4O_2 + H_2 = C_6H_6O_2$.

Preparation.—To get hydroquinone, oxidize aniline in sulphuric acid (1 part aniline, 8 parts SO_4H_2 and 25 parts H_2O) with pulverized $Cr_2O_7Na_2$ (2½ parts) until the dark precipitate, which first forms, has dissolved to a cloudy, brown liquid (containing quinone and quinhydrone). Then conduct sulphurous acid through the solution until the reduction is complete; filter, extract the hydroquinone by shaking with ether, then purify the product by recrystallization from hot water that has passed through animal charcoal (*Berichte*, 19, 1467), and contains sulphur dioxide.

Hydroquinone is dimorphous, crystallizes in monoclinic leaflets and hexagonal prisms, which melt at 169°, and sublime in shining leaflets; it decomposes when quickly heated. It dissolves readily in water (in 17 parts at 15°), alcohol and ether. It forms crystalline compounds with H_2S and SO_2; these are decomposed by water. Ammonia colors the aqueous solution reddish-brown. It is only in the presence of ammonia that lead acetate produces a precipitate in the solution of hydroquinone. Oxidizing agents (like ferric chloride) convert hydroquinone into quinone; quinhydrone is an intermediate product.

Hydroxylamine and hydroquinone form quino-dioxime, by the absorption of two hydrogen atoms (*Berichte*, 22, 1283).

Methylhydroquinone, $C_6H_4{<}\begin{matrix}O.CH_3\\ OH\end{matrix}$, is formed along with hydroquinone in the decomposition of arbutin with acids or emulsin; and from hydroquinone by heating it with caustic potash, and methyl iodide or potassium methyl sulphate (*Berichte*, 14, 1989). It crystallizes from hot water in hexagonal plates, melts at 53°, and boils at 243°. The *dimethyl ether*, $C_6H_4(O.CH_3)_2$, melts at 56°, and boils at 205°. The *diethyl ether* melts at 66°, and boils at 247°.

We obtain the hydroquinone halogen substitution products by direct substitution, or from the substituted quinones and arbutins; and by the addition of HCl or HBr to quinone: $C_6H_4O_2 + HCl = C_6H_3Cl(OH)_2$ (*Annalen*, 201, 105, and 210, 133). Two dinitro products are obtained by the nitration of diethylhydroquinone. They can be reduced to two *diamidohydroquinones*, $C_6H_2(NH_2)_2(OH)_2$ (*Berichte*, 23, 1211).

When chloranil (tetrachlorquinone) is digested with a diluted solution of primary sodium sulphite, we get at first tetrachlor-hydroquinone, but later two Cl-atoms are replaced by sulpho-groups. The aqueous solution of the resulting dichlorhydroquinone disulphonic acid, $C_6Cl_2\left\{\begin{matrix}(OH)_2\\ (SO_3H)_2\end{matrix}\right.$, is colored indigo-blue by ferric chloride. When its alkaline solution is exposed it oxidizes to *potassium euthiochronate*, $C_6(OH)_2\left\{\begin{matrix}O_2\\ (SO_3K)_2\end{matrix}\right.$. This is a quinone-like compound.

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(2) **Dioxytoluenes**, $C_6H_3(CH_3)(OH)_2$. Four of the six possible isomerides are known. For their reactions see *Berichte*, 15, 2995.

1. **Orcin, Orcinol**, $C_6H_3(CH_3)(OH)_2$ (1, 3, 5), is found in many lichens of the variety *Roccella* and *Leconora*, partly free and

partly as orsellic acid or erythrine, and is obtained from these acids either by dry distillation or by boiling with lime:—

$$\underset{\text{Orsellic Acid.}}{C_7H_5(OH)_2.CO_2H} = \underset{\text{Orcinol.}}{C_7H_6(OH)_2} + CO_2:$$

It is obtained by fusing the extract of aloes with caustic potash. It can be prepared synthetically from dinitro-paratoluidine and various other toluene derivatives by the alteration of their side groups (*Berichte*, 15, 2992). It crystallizes in colorless, six-sided prisms, containing one molecule of water. It dissolves easily in water, alcohol and ether, and has a sweet taste. It melts at 56°, when it contains water, but gradually loses this, and melts (dried in the dessicator) at 107°. It boils at 290°. Lead acetate precipitates its aqueous solution; ferric chloride colors it a *blue violet*. Bleaching lime causes a rapidly disappearing dark violet coloration. It yields azo-coloring substances with diazo-compounds, and therefore has the 2OH-groups in the meta-position (p. 643). It does not form a fluoresceïn with phthalic anhydride (p. 691).

The orcinol hydroxyl-groups can be replaced by acid and alcohol radicals. The *dimethyl ether*, $C_7H_6(O.CH_3)_2$, is a liquid, boils at 244°, and when oxidized with MnO_4K yields the dimethyl ether of symmetrical dioxybenzoic acid. See *Berichte*, 20, 1608, for dinitroso-orcin.

On allowing its ammoniacal solution to stand exposed to the air orcinol changes to orceïn, $C_{28}H_{24}N_2O_7$ (*Berichte*, 23, Ref. 647), which separates out in the form of a reddish-brown amorphous powder. Orceïn forms red lac-dyes with metallic oxides. It is the chief constitutent of the coloring matter *archil*, which originates from the same lichens as orcinol through the action of ammonia and air. *Litmus* is produced from the lichens *Roccella* and *Leconora*, by the action of ammonia and potassium carbonate. The concentrated blue solution of the potassium salt, when mixed with chalk or gypsum, constitutes the commercial litmus.

2. **Iso-orcin**, $C_6H_3(CH_3).(OH)_2$ (1, 2, 4—CH_3 in 1) (Cresorcin, γ-orcin), is obtained by fusing α-toluene disulphonic acid with KOH; also from nitro-paratoluidine, α-toluylene diamine and amido-*o*-cresol (*Berichte*, 19, 136). It forms soluble needles, melting at 104°, and boiling at 270°. It gives a *violet* coloration with ferric chloride, and forms a fluoresceïn with phthalic anhydride.

3. **Homopyrocatechin**, $C_6H_3(CH_3)(OH)_2$ (1, 3, 4—CH_3 in 1), is formed from its methyl ether, creosol, when heated with hydriodic acid, and by the distillation of homoprotocatechuic acid. It has been synthetically prepared from metanitro-para-toluidine (*Berichte*, 15, 2983). It is a non-crystallizable syrup; otherwise it is like pyrocatechin. It reduces Fehling's solution and a silver solution, even in the cold, and is colored *green* by ferric chloride.

Its *monomethyl ether* is the so-called **Creosol**, $C_6H_3(CH_3)\left\langle\begin{matrix}O.CH_3 & (3)\\ OH & (4)\end{matrix}\right.$, formed from guaiacum resin and is found in beech-wood tar.

That fraction of the beech-wood tar (creasote p. 667), boiling at 220°, consists chiefly of creosol and phlorol. Potassium-creosol is precipitated on adding alcoholic potash to the ethereal solution; potassium phlorol remains dissolved (*Berichte*, 10, 57; 14, 2010).

Creosol boils at 220°, and is very similar to guaiacol (p. 690). It reduces silver nitrate on warming, and in alcoholic solution is colored a dark green by ferric chloride.

It yields an *acetate* with acetic acid. Vanillinic acid may be obtained from the acetate by oxidizing the latter with potassium permanganate, and saponifying with caustic potash. Its *methyl ether*, $C_6H_3(CH_3)(O.CH_3)_2$ (methyl creosol, dimethyl-homo-pyrocatechin), boils at 214–218°, and when oxidized with potassium permanganate yields dimethyl-protocatechuic acid. The relations of these substances are seen in the following formulas (see Vanillin):—

$$C_6H_3\begin{cases}CH_3 & (1)\\ O.CH_3 & (3)\\ OH & (4)\end{cases} \qquad C_6H_3\begin{cases}CO_2H\\ O.CH_3\\ OH\end{cases} \qquad C_6H_3\begin{cases}CO_2H\\ OH\\ OH\end{cases}$$

Creosol. Vanillinic Acid. Protocatechuic Acid.

4. **Toluhydroquinone**, $C_6H_3(CH_3)(OH)_2$ $(1, 4, CH_3)$, is produced by the reduction of toluquinone (p. 704) with sulphurous acid, and from nitro-*o* toluidine (*Berichte*, 15, 2981). It consists of needles dissolving easily in water, alcohol and ether, and melting at 124°. It resembles hydroquinone very much, and with toluquinone yields a quinhydrone. Caustic soda colors it bluish-green, then dark brown.

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p-**Xylohydroquinone**, $C_6H_2(CH_3)_2(OH)_2$, Dioxyparaxylene (1, 4, 2, 5), results on the reduction of xylo-quinone (p. 704), and is identical with so-called *hydrophloron*, obtained from phloron (*ibid*). It crystallizes from hot water in pearly leaflets, melting at 212°.

p-**Xylo-orcinol**, $C_6H_2(CH_3)_2(OH)_2$ (1, 4, 3, 5) is obtained from *m*-dinitroparaxylene (*Berichte*, 19, 2318). It crystallizes from water in prisms, melting at 163° and boiling at 277–280°. In ammoniacal air it rapidly acquires a *red* color. It is identical with *beta-orcinol*, obtained from various lichen acids (usninic acid) by distillation.

Mesorcin, $C_6H(CH_3)_3(OH)_2 = C_9H_{12}O_2$, dioxymesitylene, from dinitromesitylene, sublimes in shining leaflets, melts at 150°, and distils at 275°. When boiled with a ferric chloride solution, a methyl group splits off and oxyxyloquinone results (p. 704).

Thymo-hydroquinone, $C_{10}H_{12}(OH)_2 = C_6H_2(CH_3)(C_3H_7)(OH)_2$, has been obtained by the reduction of thymoquinone, and forms four-sided, shining prisms, melting at 139°.

TRIHYDRIC PHENOLS.

$$C_6H_3(OH)_3\begin{cases}\text{Pyrogallic Acid} & (1, 2, 3)\\ \text{Phloroglucin} & (1, 3, 5)\\ \text{Oxyhydroquinone} & (1, 2, 4).\end{cases}$$

1. **Pyrogallic Acid**, $C_6H_6O_3$, **Pyrogallol**, is formed by heating gallic acid alone, or better, with water, to 210°:—

$$C_6H_2\begin{cases}(OH)_3\\ CO_2H\end{cases} = C_6H_3(OH)_3 + CO_2;$$

and by fusing the two parachlorphenol-disulphonic acids and hæmatoxylin with potassium hydroxide. It forms white leaflets or needles, melts at 115°, and sublimes when carefully heated. It dissolves readily in water, with more difficulty in alcohol and ether. Its alkaline solution absorbs oxygen very energetically, turns brown and decomposes into carbon dioxide, acetic acid and brown substances. Pyrogallol quickly reduces salts of mercury, silver and gold with precipitation of the metals, while it is oxidized to acetic and oxalic acids. Ferrous sulphate containing ferric oxide colors its solution blue, ferric chloride red. Lead acetate precipitates white, $C_6H_6O_3.PbO$. An iodine solution imparts a purple-red color to an aqueous or alcoholic pyrogallol solution. Gallic and tannic acids react similarly.

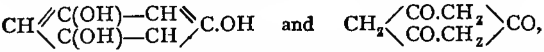
Acetyl chloride converts pyrogallol into its *triacetyl ester*, $C_6H_3.(O.C_2H_3O)_3$, which is not very soluble in water. The *dimethyl ether*, $C_6H_3(O.CH_3)_2.OH$, is found in that fraction of beech-wood tar boiling at 250–270°. Separated in a pure form from its benzoyl compound it crystallizes in white prisms, melting at 51–52°, and boiling at 253°. When heated with hydrochloric acid it breaks up into pyrogallol and methyl chloride. Different oxidizing agents (potassium bichromate and acetic acid) convert it into *cœrulignone*, a diphenyl derivative. When the *acetyl derivative* of the dimethyl ether is oxidized, the acetyl group separates and the quinone compound, $C_6H_2(O.CH_3)_2O_2$, results. The *triethyl ether* is formed on heating pyrogallol with caustic potash and potassium ethyl sulphate, also from triethyl-pyrogallo-carboxylic acid (see this). It melts at 39°. Bromine converts it into *xanthogallol*, $C_{18}H_{14}Br_{14}O_6$ (*Berichte*, 21, Ref. 626). The *trimethyl ether* melts at 47°, and boils at 235° (*Berichte*, 21, 607, 2020).

2. **Phloroglucin**, $C_6H_3(OH)_3$ (1, 3, 5), is obtained from different resins (catechu, kino), on fusion with caustic potash; by the decomposition of phloretin and quercetin, hesperidine, and other glucosides; by the fusion of phenol, resorcinol, orcin or benzene trisulphonic acid with sodium hydroxide; also by the saponification and decomposition of synthetically prepared phloroglucin-tricarboxylic ester, $C_6(OH)_3.(CO_2.C_2H_5)_3$ (p. 566).

It is most easily made by fusing resorcinol with caustic soda (*Berichte*, 12, 503; 14, 954). It crystallizes in large, colorless prisms with $2H_2O$; these effloresce in the air. It loses all its water of crystallization at 110°, melts at 218°, and sublimes without decomposition. It has a sweetish taste, and dissolves readily in water, alcohol and ether. Lead acetate does precipitate it; ferric chloride colors its solution a *dark violet.*

Chlorine oxidizes phloroglucin to dichloracetic acid and tetrachloracetone (p. 566). One of the first intermediate products is hexachlor-triketo-hexamethylene (p. 703) (*Berichte*, 22, 1469). For the action of bromine see *Berichte*, 23, 1706.

Phloroglucin, in most of its reactions (see *Berichte*, 23, 269), conducts itself like a trihydric phenol, $C_6H_3(OH)_3$; on the other hand it unites with 3 molecules of hydroxylamine to form a *trioxime* (see below), hence it may be considered a triketone—*triketo-hexamethylene* (p. 567) (*Berichte*, 19, 159). The two formulas—



$$\mathrm{CH}\begin{matrix}\diagup\!\!\diagup \mathrm{C(OH)—CH} \diagdown\!\!\diagdown \\ \diagdown \mathrm{C(OH)—CH} \diagup \end{matrix}\mathrm{C.OH} \quad \text{and} \quad \mathrm{CH_2}\begin{matrix}\diagup \mathrm{CO.CH_2} \diagdown \\ \diagdown \mathrm{CO.CH_2} \diagup \end{matrix}\mathrm{CO},$$

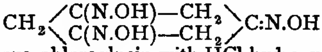
of which the first is derived from tertiary, the second from the secondary benzene ring (p. 568) are either tautomeric, or the latter represents the unstable or pseudo-form (p. 50).

Normal ethers of phloroglucin have been obtained by heating it with alcohol and hydrochloric acid gas, or with ethyl iodide. The *trimethyl ether*, $C_6H_3(OCH_3)_3$, melts at 52°, and boils at 255° (*Berichte*, 21, 603). Its triethyl ether, $C_6H_3(O.C_2H_5)_3$, melts at 43°.

The *dibutyryl ester* occurs in the root of *Aspidium filix*. It is a crystalline substance, which yields phloroglucin and butyric acid when fused with KOH (*Berichte*, 22, 463, Ref. 806).

Phloroglucin-triacetyl Ester, $C_6H_3(O.C_2H_3O)_3$, melts at 106°. When phloroglucin is heated with caustic potash and alkyl iodides it yields ethers, derived from the isomeride of triketo-hexamethylene. They are insoluble in the alkalies. Hexamethyl-phloroglucin, $C_6(CH_3)_6O_3$, melts at 80° (*Berichte*, 22, Ref. 670; 23, 20).

Phloroglucin Trioxime, $C_6H_9N_3O_3$ =



$$CH_2\left\langle\begin{matrix}C(N.OH)—CH_2\\C(N.OH)—CH_2\end{matrix}\right\rangle C{:}N.OH$$

(see above), separates, on standing, from aqueous phloroglucin with HCl-hydroxylamine (3 molecules) and potassium carbonate. It is a crystalline powder. At 140° it becomes black, and at 155° explodes violently.

3. **Oxyhydroquinone**, $C_6H_3(OH)_3$ (1, 2, 4), is produced on fusing hydroquinone with KOH (together with tetra- and hexaoxy-diphenyl. *Berichte*, 18, Ref. 24). It is crystalline, very soluble in alcohol and ether, and in aqueous solution soon acquires a dark color. It melts at 140.5°. Ferric chloride colors it a dark greenish-brown. Its **tri-ethyl ether**, $C_6H_3(O.C_2H_5)_3$, is obtained from trioxyethyl benzoic acid (from æsculetin). It can also be prepared by ethylating ethoxy-hydroquinone. It melts at 34° (*Berichte*, 20, 1133). The **trimethyl ether**, $C_6H_3(O.CH_3)_3$, from methoxy-quinone (p. 702), boils at 247°.

Methyl pyrogallol, $C_6H_2(CH_3)(OH)_3$, and **Propyl pyrogallol**, $C_6H_2(C_3H_7)(OH)_3$, occur in beech-wood tar as dimethyl ethers (p. 667); the latter is identical with so-called *picamar*.

TETRA- AND POLY-HYDRIC PHENOLS.

Tetraoxybenzenes.

(1) Symmetrical **Tetraoxy-benzene**, $C_6H_2(OH)_4$ (1, 2, 4, 5), is obtained by reducing dioxyquinone with stannous chloride. It crystallizes in silvery needles, melting at 215–220°. It is oxidized to dioxyquinone (p. 702) when exposed, in acid solution, to the air, or by ferric chloride (*Berichte*, 21, 2374).

Dichlortetraoxy-benzene, $C_6Cl_2(OH)_4$ (the Cl-atoms in 1, 4), results in the reduction of chloranilic acid (p. 701) with sodium amalgam, or with tin and hydrochloric acid, and by heating it with sulphurous acid. It forms colorless needles, dissolving readily in water. It is reoxidized to chloranilic acid on exposure to moist air.

Diamido-tetraoxy-benzene, $C_6(NH_2)_2(OH)_4$ (the NH_2 groups in 1, 4), is obtained by reducing nitranilic acid (p. 701) with tin and hydrochloric acid. It separates as HCl-salt, $C_6(OH)_4.(NH_2\ HCl)_2$, in long, colorless needles (*Berichte*, 18, 503; 19, 2727). Ferric chloride and other oxidizing agents convert it into *diimido-dioxy-quinone*, $C_6(NH_2)_2O_2(OH)_2$, a black, crystalline precipitate, which nitric acid oxidizes to triquinoyl (p. 703).

(2) Unsymmetrical **Tetraoxybenzene**, $C_6H_2(OH)_4$ (1, 3, 4, 5), is only known in certain ethers. The *dimethyl ether*, $C_6H_2(O.CH_3)_2(OH)_2$, is prepared by reducing dimethyl dioxyquinone with tin chloride. It forms brilliant crystals, melting at 158°. Caustic potash and methyl iodide convert it into the *tetramethyl*

ether, $C_6H_2(O.CH_3)_4$, melting at 47° and boiling at 271° (*Berichte*, 21, 609; 23, 2288).

(3) Adjacent Tetraoxybenzene, $C_6H_2(OH)_4$ (1, 2, 3, 4), with the two hydrogen atoms in the ortho-position, is *apionol*, the parent substance of *apiol*, the methylene dimethyl ether of allyl apionol, $C_6H(C_3H_5)(OH)_4$ (*Berichte*, 23, 2293).

Dimethyl Apionol, $C_6H_2(O.CH_3)_2(OH)_2$, is formed by heating apiolic acid with caustic potash to 180°. It melts at 106°, and boils at 298°. The introduction of methyl yields **Tetramethyl Apionol**, $C_6H_2(O.CH_3)_4$, melting at 81° (*Berichte*, 22, 2482). **Methylene-dimethyl Apionol**, $C_6H_2(O_2:CH_2)(O.CH_3)_2$, **Apione**, is formed when apiolic acid loses carbon dioxide. It melts at 79°, and is volatile with steam (*Berichte*, 21, 1630, 2129).

Hexoxybenzene, $C_6(OH)_6 = C_6H_6O_6$, is obtained from triquinoxyl (p. 703) by reduction with stannous chloride and hydrochloric acid. It separates in the form of small, grayish-white needles, which acquire a reddish-violet color on exposure to the air. They are not fusible, but decompose about 200°. Concentrated nitric acid oxidizes it to triquinoyl.

It forms the **hexacetyl derivative**, $C_6(O.C_2H_3O)_6$, when heated with acetic acid and sodium acetate. It is a crystalline mass, melting at 203° (*Berichte*, 18, 506).

The *hexapotassium* salt of hexaoxybenzene, $C_6O_6K_6$, is the so-called *potassium carbon monoxide*, which results upon conducting carbon monoxide over heated potassium. It is obtained in the preparation of potassium. Dilute hydrochloric acid, acting upon the fresh mass, yields hexaoxybenzene (*Berichte*, 18, 1833).

Quercite and Pinite seem to be *pentahydric* phenols of hexahydrobenzene, $C_6H_6.H_6$.

Quercite, $C_6H_{12}O_5 = C_6H_7(OH)_5$, occurs in acorns. It can be extracted from them by means of water. Different hexoses accompany it, but they can be destroyed by fermentation. It has a sweet taste, dissolves in 8 parts of water, and crystallizes in hard prisms, melting at 235°. Five hydroxyls present in it can be replaced by acidyls. If quercite be heated alone or together with hydriodic acid various benzene products are obtained. Nitric acid oxidizes it to mucic and trioxyglutaric acids (same as sorbinose and arabinose) (*Berichte*, 22, 518).

α- and β-**Pinite**, $C_6H_{12}O_5$ or $C_7H_{14}O_6$, occur in the resin of *Pinus lambertina*. The first melts about 150°, the second at 187°. Both yield rhodizonic acid when evaporated with nitric acid (*Berichte*, 23, 25).

Inosite, $C_6H_{12}O_6 + 2H_2O$, **Phaseomannite**, is a *hexahydric* phenol of hexahydrobenzene. It occurs in the muscles of the heart, and in different plants (unripe peas and beans). It forms large crystals, that weather on exposure and then melt at 225°. There are six hydroxyl-groups in it that can be replaced by acid radicals. If heated with hydriodic acid to 170°, it yields benzene and triiodophenol. Nitric acid oxidizes it to two dioxy-, one tetraoxyquinone, and rhodizonic acid (*Berichte*, 20, Ref. 478; 23, Ref. 26).

Phenose, is a hexahydric phenol of hexahydrobenzene, $C_6H_6(OH)_6$. It has been obtained by the action of a soda solution (*Annalen*, 136, 323) upon the addition product of benzene with three molecules of hypochlorous acid, $C_6H_6\left\{\begin{matrix}Cl_3\\(OH)_3\end{matrix}\right.$. It is an amorphous, readily soluble substance, deliquescing in the air. It is very much like the glucoses, has a sweet taste and reduces Fehling's solution—but is not capable of fermentation.

QUINONES.

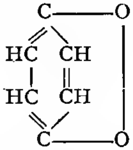
This is the designation ascribed to all derivatives of benzene in which 2H-atoms are replaced by 2O-atoms. They are mostly produced by the direct oxidation of benzenes, especially the condensed varieties (naphthalene, anthracene, chrysene, phenanthrene), with chromic acid in glacial acetic acid. These compounds, however, do not possess uniform character, hence various quinone groups are noted.

The *true quinones* or *para-quinones*, whose prototype is ordinary quinone or benzoquinone, $C_6H_4O_2$, are yellow colored, volatile compounds, having a peculiar, penetrating quinone odor, and are readily volatilized with steam. Reducing agents (SO_2, conc-HI) easily convert them, with absorption of 2H-atoms, into the corresponding colorless dioxy-compounds (hydroquinones):—

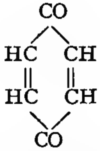
$$C_6H_4(O_2) + H_2 = C_6H_4(OH)_2, \text{ Hydroquinone (1, 4).}$$

Hence they oxidize readily, and may be compared to the peroxides (like acetyl peroxide $(C_2H_3O)_2O_2$). The two oxygen atoms take the para-position in the benzene nucleus, and the para-quinones therefore are readily produced by oxidation of the para-di-derivatives of the benzenes.

It is usually supposed that in the ordinary quinones the 2O-atoms are linked by one valence to each other; it is, however, possible, that they ought to be considered as di-ketones having 2CO-groups:—



or



The fact that in the different reactions the 2O-atoms are invariably separated by only two monovalent atoms or groups (in the action of PCl_5) forming normal benzene derivatives, C_6X_6; furthermore, the simple relations of the quinones to the quinone-chlorimides and indophenols (p. 705), argue for the first view.

According to the second formula the quinones are derivatives of a reduced benzene nucleus, *dihydrobenzene*, C_6H_8 (p. 568), and are to be termed *diketo-dihydrobenzenes*. In support of their ketone nature we have their ability to yield quinoximes with one molecule of hydroxylamine (these are identical with the nitrosophenols). A stronger proof is the production of quinon-dioxime, HO.N:  $C\left\langle\begin{matrix}CH = CH\\CH = CH\end{matrix}\right\rangle C{:}N.OH$, by the union of quinone with two molecules of hydroxylamine (p. 675). The production of bromine additive products might be an additional argument (*Jr. pr. Ch.*, 42, 61; *Berichte*, 23, 3141).

Yet, the quinones of the benzene series are not capable of combining with phenylhydrazine, but are only reduced by it, while the naphthaquinones and phenanthraquinones form hydrazides (*Berichte*, 18, 786).

Another series of quinones (β naphthaquinone, anthraquinone, phenanthraquinone) must be considered true diketones (with 2CO-groups). They are non-volatile and odorless, and are either *para-diketones* (like anthraquinone) or *ortho-diketones* (*e.g.*, β naphthaquinone and phenanthraquinone). Sulphurous acid reduces the latter to the corresponding hydroquinones; they form anhydro-compounds with the aldehydes and ammonia.

There exist, finally, the quinones with two nuclei, *e.g.*, cœrulignone, derived from diphenyl. In these the 2O-atoms link two benzene nuclei.

Quinone, $C_6H_4O_2$, Benzoquinone, was first obtained by distilling quinic acid with MnO_2 and sulphuric acid. It is formed from many benzene compounds, especially those di-derivatives belonging to the para-series (*e.g.*, para-phenylene-diamine, amidophenol, phenol sulphonic acid and sulphanilic acid), when they are oxidized with MnO_2 and sulphuric acid, or with a dilute chromic acid mixture. Benzidine, $C_{12}H_8(NH_2)_2$, likewise yields a considerable quantity of quinone. Hydroquinone is oxidized to quinone even on boiling with a ferric chloride solution. It is, however, best prepared (according to Nietzki) by oxidizing aniline with chromic acid.

Preparation.—Oxidize aniline in sulphuric acid solution, just as was done in the case of hydroquinone (p. 691), adding, however, a little more sodium bichromate to effect the complete oxidation to quinone, then extract with ether. A better course is to prepare the quinone from hydroquinone already prepared; to this end dissolve the latter in as little water as possible, add two parts of sulphuric acid, and while cooling introduce the sodium bichromate solution, until the precipitate consists of pure yellow quinone. This is filtered at once (*Berichte*, 19, 1468; compare *Berichte*, 20, 2283).

Quinone crystallizes in golden-yellow prisms, melts at 116°, and sublimes at medium temperatures, in shining needles. Its vapor density confirms the formula $C_6H_4O_2$. It possesses a peculiar, penetrating odor, distils readily with steam, and dissolves easily in hot water, alcohol and ether. It turns brown on exposure to sunlight. Reducing agents (SO_2, Zn and HCl) convert it first into quinhydrone and then into hydroquinone. PCl_5 changes it to para-dichlorbenzene, $C_6H_4Cl_2$.

Quinone forms chlor- and brom-hydroquinone with concentrated hydrochloric and hydrobromic acids (p. 692). It also unites with two molecules of acetyl chloride to form diacetyl-chlorhydroquinone, $C_6H_4O_2 + 2C_2H_3OCl = C_6H_3Cl(O.C_2H_3O)_2 + HCl$ (*Berichte*, 16, 2096). Quinone yields *quinoxime*, $C_6H_4O:N.OH$ (*p*-nitrosophenol) and quinon-dioxime, $HO.N:C_6H_4:N.OH$ (p. 675), with hydroxylamine hydrochloride. All true para quinones show a like reaction in acid solution. Their dioximes do not form anhydrides. They unite with acetic anhydride to diacetyl compounds. Di-nitrosobenzenes are produced by the oxidation of their alkaline solutions (also on exposure to the air). Nitric acid oxidizes them to di-nitrobenzenes (*Berichte*, 21, 428). *Orthoquinones*, or ortho-diketones (p. 698), and their monoximes, when in alkaline solution, unite with hydroxylamine to form *dioximes*, capable of yielding anhydrides (*Berichte*, 23, 2815).

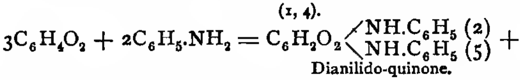
The quinone monoximes and phenylisocyanate unite and yield carbanilides. The dioximes combine with two molecules of $C_6H_5.N:CO$, and form di-carbanilides.

They are partly changed to anhydrides (*Berichte*, 22, 3105). Of the substituted quinones, only those quinone or CO-groups react with phenylisocyanate, in which the adjacent positions (ortho) *are not replaced* (*Berichte*, 21, 3316, 3493).

When the primary amines and anilines act upon the quinones, the following may occur:—

(1) Either the quinone oxygen is replaced by the imide-group : NR, with the production of *quinone-imides* and *quinone-diimides*, *e.g.*, $C_6H_4O{:}N.C_6H_5$ and $C_6H_5.N{:}C_6H_4{:}N.C_6H_5$.

(2) Or, the hydrogen of benzene is substituted. Then *anilido-quinones* result. At the same time, quinone is reduced to hydroquinone (*Berichte*, 18, 785):—



$$3C_6H_4O_2 + 2C_6H_5.NH_2 = \underset{\text{Dianilido-quinone.}}{\overset{(1,\,4).}{C_6H_2O_2}\begin{matrix}\diagup NH.C_6H_5\ (2)\\ \diagdown NH.C_6H_5\ (5)\end{matrix}} + 2C_6H_4(OH)_2.$$

Such compounds are readily obtained from oxy-quinones. Again, the oxy-quinone imides, $R\begin{matrix}\diagup\!\!\diagup NH\\ \diagdown OH\end{matrix}$, and the quinone-amides, $R\begin{matrix}\diagup\!\!\diagup O\\ \diagdown NH_2\end{matrix}$, are sometimes tautomeric (*Berichte*, 23, 897).

Dianilido-quinone, $C_{18}H_{14}N_2O_2$, Quinone-anilide, is formed by boiling quinone with aniline and alcohol. It forms brownish-violet scales, with metallic lustre (*Berichte*, 16, 1556). In the presence of acetic acid the product is Dianilido-quinone-anilide, $C_6H_2O(N.C_6H_5)(NH.C_6H_5)_2$ (*Berichte*, 18, 787), while by fusing quinone with aniline or aniline hydrochloride, we obtain Dianilido-quinone-dianilide, $C_6H_2(N.C_6H_5)_2.(NH.C_6H_5)_2$ (1, 4, 2, 5) $= C_{30}H_{24}N_4$, Azophenine (*Berichte*, 21, 683; 21, Ref. 656).

The latter is also produced by the action of aniline upon amidoazobenzene, *p*-nitrosophenol and *p*-nitrosodiphenylamine (*Berichte*, 20, 2480). It consists of garnet-red needles, melting at 241°. It dissolves with a violet color in oil of vitriol. It becomes blue in color at 300°. It changes to *fluorindin* when heated (*Berichte*, 23, 2791). The induline dyes are intimately related to azophenine.

The quinones react similarly with the phenylene diamines (*Berichte*, 23, 2793).

Phenylhydrazine reduces the quinones of the benzene series to hydroquinones, whereas the naphthaquinones and phenanthraquinone yield hydrazones.

The phenols and quinones form compounds containing 2 molecules of the monovalent phenols (*Annalen*, 215, 134). Phenoquinone, $C_6H_4O_2.2C_6H_5.OH$, crystallizes in red needles, melting at 71°. It is very volatile. Caustic potash colors it blue, and baryta water green. An analogous compound is—

Quinhydrone, $C_{12}H_{10}O_4 = C_6H_4O_2.C_6H_4(OH)_2$. This is produced by the direct union of quinone with hydroquinone. It appears as an intermediate product in the reduction of quinone or in the oxidation of hydroquinone. It consists of green prisms or leaflets with metallic lustre, melts readily, and dissolves in hot water with a brown, in alcohol and ether with a green, color. When it is boiled with water it decomposes into hydroquinone and quinone, which distils over. It is changed by oxidation to quinone, and by reduction to hydroquinone.

Chlor- and *brom-*quinones are obtained by the substitution of quinone or by the oxidation of substituted hydroquinones (p. 692) with nitric acid.

Trichlorquinone, $C_6HCl_3(O_2)$, is produced, together with *tetrachlorquinone;* it consists of large, yellow plates, melting at 166°. It forms tetrachlorhydroquinone, $C_6Cl_4(OH)_2$, by heating with fuming hydrochloric acid. Fuming nitric acid oxidizes this product to tetrachlorquinone.

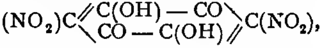
Tetrachlorquinone, $C_6Cl_4(O_2)$, **Chloranil**, is obtained, together with trichlorquinone from many benzene compounds (aniline, phenol, isatin) by the action of chlorine or potassium chlorate and hydrochloric acid. Its production from symmetrical tetrachlorbenzene (p. 582) by boiling with nitric acid is theoretically interesting.

In order to prepare it, gradually add a mixture of phenol (1 part) with ClO_3K (4 parts) to concentrated hydrochloric acid, diluted with an equal volume of water, and apply a gentle heat. At first red crystals separate out, but on the addition of more ClO_3K these become yellow. The crystalline mass consists of tri- and tetra-chlorquinone. To effect their separation, they are changed by SO_2 to hydroquinones (tetrachlorhydroquinone is insoluble in water) and the latter oxidized with nitric acid (*Berichte*, 10, 1792, and *Annalen*, 210, 174).

Chloranil consists of bright golden leaflets, insoluble in water, but soluble in hot alcohol and ether. It sublimes about 150°, in yellow leaflets. PCl_6 converts it into C_6Cl_6. It oxidizes and serves as an oxidizing agent in the manufacture of coloring matters. Chloranil dissolves with a purple-red color in dilute KOH, forming *potassium chloranilate*, $C_6Cl_2(O_2)(OK)_2 + H_2O$, which crystallizes in dark red needles, not very soluble in water. Acids set free chloranilic acid, $C_6Cl_2(O_2)(OH)_2 + H_2O$, which consists of red, shining scales. Aqueous ammonia converts chloranil into *chloranilamide*, $C_6Cl_2(O_2)(NH_2)_2$, and *chloranilamic acid*, $C_6Cl_2(O_2).(NH_2)OH$.

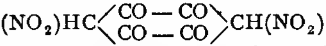
The brom-quinones are perfectly analogous to the chlorine derivatives. *Tetrabromquinone*, **Bromanil**, $C_6Br_4O_2$, is obtained by heating phenol (1 part) with 10 parts of bromine and 3 parts of iodine in 50 parts of water. It consists of golden-yellow, shining leaflets or thick plates, which melt and sublime. By dissolving tetra- or tri-bromquinone in dilute caustic potash we obtain the potassium salt of *bromanilic acid*, $C_6Br_2(O_2)(OH)_2$, crystallizing in dark red needles or bronze-colored leaflets. Bromanilic acid is formed by allowing bromine to act upon dioxyquinone-dicarboxylic acid, $C_6(O_2)(OH)_2(CO_2H)_2$, and it, therefore, contains two bromine atoms in the para-position (*Berichte*, 20, 1303 and 1997).

Nitranilic Acid, $C_6(NO_2)_2O_2(OH)_2 =$



$$(NO_2)C\begin{matrix}\diagup\!\!\diagup C(OH)-CO\diagdown \\ \diagdown CO-C(OH)\diagup\!\!\diagup\end{matrix}C(NO_2),$$

or

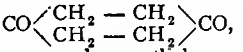


$$(NO_2)HC\begin{matrix}\diagup CO-CO\diagdown \\ \diagdown CO-CO\diagup\end{matrix}CH(NO_2)$$

(see *Berichte*, 22, Ref. 292), analogous to brom- and chloranilic acid, is formed from quinone and hydroquinone with nitrous acid; more readily from diacetyl-hydroquinone with fuming nitric acid, or by the action of sodium nitrite upon chloranil (*Berichte*, 22, Ref. 292). It also results from dioxyterephthalic and dioxyquinone-terephthalic acids by the action of fuming nitric acid; the two NO_2- and OH-groups are, therefore, in the para-position (*Berichte*, 19, 2398 and 2727). It crystallizes with water in golden yellow needles or plates, melts in its water of crystallization, becomes anhydrous at 100°, and detonates at 170° without melting. The *potassium salt*, $C_6(NO_2)_2(O_2)(OK)_2$, forms yellow needles, soluble with difficulty in water. When nitroanilic acid is reduced it yields diamidotetroxybenzene (p. 696).

We may look upon chlor-, brom- and nitranilic acids as derivatives of dioxyquinone, $C_6H_2(O_2)(OH)_2$.

Diketo-hexamethylene, $C_6H_8O_2 =$



$$CO\begin{matrix}\diagup CH_2-CH_2\diagdown \\ \diagdown CH_2-CH_2\diagup\end{matrix}CO,$$

Tetrahydroquinone, is a derivative of hexahydrobenzene or hexamethylene. It results upon expelling two molecules of carbon dioxide from succino-succinic acid. It forms colorless crystals, melting, at 78° (*Berichte*, 22, 2170). It forms a *dioxime* with hydroxylamine, $C_6H_6(N.OH)_2$. Sodium and alcohol reduce this to *p-diamido hexamethylene*, $C_6H_6(NH_2)_2$. Phenylhydrazine converts tetrahydroquinone into a *dihydrazone*. Hydrocyanic acid converts it into the dicyanhydrin, $C_6H_8(OH)_2(CN)_2$, etc. (*Berichte*, 22, 2176).

OXYQUINONES AND POLYQUINOYLS.

Oxy-quinone, $C_6.H_3(O_2).OH$.
Dioxyquinone, $C_6H_2(OH)_2O_2$.
Tetroxyquinone, $C_6(OH)_4O_2$.
Dioxydiquinoyl, $C_6(O_2)(O_2)(OH)_2$.
Triquinoyl, $C_6(O_2)_3$.

Oxy-quinone, $C_6H_3(O_2).OH$. Its *methyl ether* is produced by oxidizing *o*-amido-anisol, $C_6H_4(NH_2).O.CH_3$, with potassium permanganate and sulphuric acid. It consists of yellow needles, melting at 140°. Sulphurous acid reduces it to methyl-oxy-hydroquinone (p. 696) (*Berichte*, 21, 606).

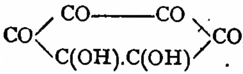
Dioxyquinone, $C_6H_2(O_2)(OH)_2$ (1, 2, 4, 5), is obtained from dioxyquinone dicarboxylic acid, $C_6(O_2)(OH)_2(CO_2H)_2$ (its sodium salt), by boiling with hydrochloric acid, by the oxidation of diamido-resorcin in alkaline solution (*Berichte*, 21, 2374; 22, 1288) and by the action of sulphuric acid upon dianilidoquinone (*Berichte*, 23, 904). It separates in small blackish-brown crystals, which sublime above 185°. It dissolves in alcohol with a deep red, in alkalies with a bright yellow color. Acids reprecipitate it in the form of a dark yellow crystalline powder. Stannous chloride reduces it to symmetrical tetraoxy-benzene (p. 696) and dianilidoquinone, $C_6H_2(O_2)(NH.C_6H_5)_2$, is produced when it is heated with aniline (p. 700). Hydroxylamine hydrochloride converts it into a *dioxime*, $C_6H_2(N.OH)_2(OH)_2$, that yields diamidohydroquinone by reduction.

Diquinoyl, $C_6H_2(O_2)(O_2)$ (1, 2, 3, 4), is not known in a free condition. Dinitroresorcin (p. 627) is its *dioxime*, $C_6H_2(O_2)(N.OH)_2$, from which hydroxylamine produces diquinoyltetroxime, $C_6H_2(N.OH)_4$ (1, 2, 3, 4) (*Berichte*, 23, 2816, 3139).

Tetraoxy-quinone, $C_6(O_2)(OH)_4$, formerly called dihydrocarboxylic acid, is obtained by oxidizing the aqueous solution of hexaoxybenzene (p. 697) by exposure to the air. It may also be obtained from diamido-dioxyquinone (*Berichte*, 21, 1853). The *disodium salt*, $C_6O_2(OH)_2(ONa)_2$, separates in metallic black needles, if the aqueous solution of hexa-oxybenzene, mixed with soda, be allowed to stand exposed to the air. When the salt is boiled with dilute hydrochloric acid, tetroxyquinone separates in black needles with a green, metallic reflex (*Berichte*, 18, 507, 1837). It is not fusible, but readily soluble in hot water and alcohol. It is a strong dibasic acid.

Dioxydiquinoyl, $C_6(O_2)(O_2)(OH)_2$, called *rhodizonic* acid, is prepared by reducing triquinoyl, $C_6(O_2)_3$, by digesting it with aqueous sulphurous acid (*Berichte*, 18, 513). It consists of colorless leaflets, very readily soluble in water; it decomposes quite rapidly in aqueous solution. The corresponding salts are obtained by saturating the aqueous solution with potassium and sodium carbonate. The *potassium salt*, $C_6O_4(OK)_2$, may also be made by washing potassium-hexaoxy-benzene (potassium carbon monoxide, p. 697) with alcohol. It forms dark blue needles, dissolving in water with an intense yellow color. The *sodium salt*, $C_6H_4(ONa)_2$, consists of violet needles, or shining octahedra (*Berichte*, 19, 1838).

Dioxy-diquinoyl is probably a para- and ortho-diketone; its two hydroxyls occupy the ortho-position with reference to each other (*Berichte*, 23, 3140):—



$$CO\left\langle\begin{matrix}CO-\!\!-\!\!-CO\\C(OH).C(OH)\end{matrix}\right\rangle CO$$

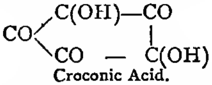
Dioxydiquinoyl.

In consequence it yields with orthotoluylene diamine (one molecule) a diazine (p. 628), from which a diquinoyl can be prepared by oxidation. This is capable of combining further with two molecules of *o*-toluylene diamine and forming a triazine- or triphenazine-derivative (*Berichte*, 20, 322).

Hexachlor-triketone, $C_6Cl_6O_3 = CCl_2\left\langle\begin{matrix}CO.CCl_2\\CO.CCl_2\end{matrix}\right\rangle CO$, is produced when chlorine acts upon a chloroform solution of phloroglucin (*Berichte*, 22, 1467). It forms colorless crystals with a disagreeable odor. It melts at 48°, and boils at 269°. Stannous chloride reduces it to trichlorphloroglucin, $C_6Cl_3(OH)_3$. Water decomposes it into dichloracetic acid, tetrachloracetone and carbon dioxide: $C_6Cl_6O_3 + 2H_2O = CHCl_2.CO_2H + CO(CHCl_2)_2 + CO_2$ (*Berichte*, 23, 230).

Triquinoyl, $C_6O_6 + 8H_2O = CO\left\langle\begin{matrix}CO-CO\\CO-CO\end{matrix}\right\rangle CO + 8H_2O$, hexaketo-hexamethylene (*Berichte*, 20, 322), results upon oxidizing dioxydiquinoyl and diamidotetroxybenzene (p. 696) with nitric acid. It is a white, micro-crystalline powder (*Berichte*, 18, 504). It melts about 95°, giving up water and CO_2. It is likewise decomposed by warming it with water to 90°. Stannous chloride reduces it to hexa-oxy-benzene, which is oxidized in alkaline solution to tetraoxyquinone, $C_6(O_2)(OH)_4$, and dioxydiquinoyl, $C_6(O_2)_2(OH)_2$ (see above).

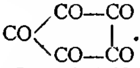
Triquinoyl, hexaoxybenzene and their derivatives, in various oxidation reactions, give off carbon dioxide and yield *croconic acid*, $C_5H_2O_5$, which by more energetic oxidation becomes leuconic acid, $C_5O_5 + 4H_2O$. Both substances are, in all probability, derivatives of pentamethylene (p. 520), and correspond to the formulas (*Berichte*, 19, 308, 772):—



$$CO\left\langle\begin{matrix}C(OH)-CO\\ \qquad\quad |\\CO - C(OH)\end{matrix}\right.$$

Croconic Acid.

and



$$CO\left\langle\begin{matrix}CO-CO\\ \qquad |\\CO-CO\end{matrix}\right.$$

Leuconic Acid.

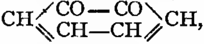
For the course of the transformation of the benzene ring into the pentamethylene ring see *Berichte*, 20, 1267 and 1617.

Croconic Acid, $C_5H_2O_5 = C_5O_3(OH)_2$, is produced by the alkaline oxidation of most of the hexa substituted benzene-derivatives, *e. g.*, hexaoxybenzene, dioxydiquinoyl, diamido-tetroxy-benzene, etc. Triquinoyl, when boiled with water, decomposes into carbon dioxide and croconic acid:—

$$C_6O_6 + H_2O = C_5H_2O_5 + CO_2.$$

Free croconic acid crystallizes with three molecules of water in sulphur-yellow leaflets; it loses its water of crystallization at 100°. It dissolves very readily in water and alcohol. Its *potassium salt*, $C_5O_5K_2 + 3H_2O$, crystallizes in orange yellow needles. When oxidized with nitric acid or chlorine the product is—

Leuconic Acid, $C_5O_6 + 4H_2O$, Pentaketo-penta-methylene, which is reconverted into croconic acid by sulphur dioxide. It is very soluble in water, but dissolves with difficulty in alcohol and ether. It crystallizes in small colorless needles. Being a pentaketo compound it unites with five molecules of hydroxylamine, forming the **penta-oxime**, $C_5(N.OH)_6$. A **tetroxime**, $C_5(N.OH)_4O$, is produced at the same time. Stannous chloride reduces these oximes to **penta-amido-pentol**, $C_5H(NH_2)_5$, and **tetra-amido-oxy-pentol**, $C_6H(OH)(NH_2)_4$ (*Berichte*, 22, 916). As a diorthoketone it unites with two molecules of toluylene-diamine and forms the *diphenazine*, $C_5O(N_2C_7H_6)_2$, which as a ketone is capable of combining with one molecule of phenylhydrazine (*Berichte*, 19, 777).

With naphthalene there is known, in addition to the ordinary α-naphthaquinone (corresponding to ordinary quinone), an isomeric β-naphthaquinone, which is an orthodiketone (CO.CO—) (p. 698). The **o-Benzoquinone**, $C_6H_4O_2$ =  $\mathrm{CH}\left\langle\begin{matrix}\mathrm{CO}-\mathrm{CO}\\ \mathrm{CH}-\mathrm{CH}\end{matrix}\right\rangle\mathrm{CH}$, corresponding to it, is only known in its halogen-derivatives.

Tetrachlor- and **Tetrabrom-o-benzoquinone**, $C_6Br_4O_2$, are produced by oxidizing tetrachlor- and tetrabrom-pyrocatechin, $C_6Br_4(OH)_2$ (1, 2), with nitric acid. Both form crystals with a garnet-red color and show a metallic lustre. The first melts at 132°; the second at 151° (*Berichte*, 20, 1778).

The homologous quinones are quite similar to benzoquinone.

Toluquinone, $C_6H_3(CH_3)O_2$, is obtained by oxidizing various amidotoluenes. It is most conveniently prepared by oxidizing *o*-toluidine (crude) with chromic acid (*Berichte*, 20, 2283), just as in the case of benzoquinone. It consists of golden yellow leaflets, melting at 67°; these are very volatile and have the quinone odor. Reduction (with SO_2) converts it into tolu-hydroquinone (p. 694). Hydroxylamine converts it into the **monoxime**, $C_6H_3(CH_3)O{:}N.OH$, identical with nitroso-*o*-cresol (p. 685), and **toluquinon-dioxime**, $C_6H_3(CH_3)(N.OH)_2$, which is also obtained from nitrosotoluidine (p. 623) (*Berichte*, 21, 733). It forms yellow needles, chars at 210°, and detonates at 234°. When it is oxidized in alkaline solution it yields dinitrotoluene. Aniline and toluquinone yield anilides (p. 700).

Xyloquinones, $C_6H_2(CH_3)_2O_2$. The three possible isomerides are known.

o-**Xyloquinone** (1, 2, O_2), is obtained from amido-*o*-xylene by oxidation with $K_2Cr_2O_7$. It sublimes in yellow needles, melting at 55° (*Berichte*, 18, 2673). *m*-**Xyloquinone** (1, 3, O_2) is obtained from amido-*m*-xylene and amidomesitylene, by the displacement of a CH_3-group (*Berichte*, 18, 1150). It melts at 73°. The oxidation of diamido- or dioxymesitylene, by chromic acid, produces oxy-*m*-xyloquinone, melting at 102°. The yellow aqueous solution is colored a deep violet by alkalies, or even by spring water.

p-**Xyloquinone**, $C_6H_2(CH_3)_2O_2$ (1, 4, O_2), results by the oxidation of *p*-xylidine, or more readily from diamido-xylene (obtained by the decomposition of amido-azo-xylidine). It is identical with *phloron*. It is most easily obtained from pseudocumidine, $C_6H_2(CH_3)_3.NH_2$, by oxidation with chromic acid (*Berichte*, 18, 1150). It consists of golden yellow needles, which resemble quinone in odor, and melt at 123°. With hydroxylamine it forms (like quinone) a *monoxime* and *dioxime* (*Berichte*, 20, 978).

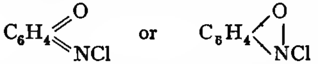
Durenequinone, $C_6(CH_3)_4O_2$ (1, 2, 4, 5, O_2), is produced by oxidizing diamidodurene with ferric chloride or sodium nitrite. It forms long yellow needles, melting at 111°.

Thymo-quinone, $C_6H_2(CH_3)(C_3H_7)O_2$, Thymoïl, is formed by oxidizing thymol or carvacrol (p. 688) with MnO_2 and H_2SO_4, or amidothymol with ferric chloride. It forms yellow plates, melts at 45.5°, and boils at 232°. By reduction it yields thymohydroquinone (p. 694). With hydroxylamine it yields a monoxime (nitrosothymol, p. 688). See *Berichte*, 22, 3268, upon iodo- and bromthymoquinone.

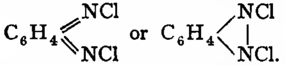
Two *Oxythymoquinones*, $C_{10}H_{11}(OH)O_2$ and *Dioxythymoquinone*, $C_{10}H_{10}(OH)_2O_2$, are produced on heating bromthymoquinone with KOH. They yield *thymodiquinone*, $C_{10}H_{10}(O_2)(O_2)$, by oxidation (*Berichte*, 23, 1391; Ref. 565).

QUINONE-CHLORIMIDES.

These are very similar to the quinones, and possess an analogous constitution (p. 698). We must regard them either as diketones or peroxides, in which oxygen is replaced by the group NCl. The latter view corresponds to the formulas:—



Quinone Chlorimide.



Quinone Dichlorimide.

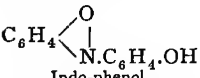
They are produced from *p*-amidophenols and *p*-phenylene diamines (their HCl-salts) by oxidation with an aqueous solution of bleaching lime. The monochlorimides form the indophenol coloring matters (see below) with phenols and tertiary anilines.

Quinone Chlorimide, $C_6H_4(ONCl)$, produced from HCl-para-amidophenol with bleaching lime (*Journ. pr. Chem.* 23, 435), forms golden yellow crystals, which melt at 85°, volatilize readily with steam and smell like quinone. It is easily soluble in hot water, alcohol and ether. Reducing agents (also H_2S) convert it into *p*-amidophenol. When boiled with water it decomposes into NH_4Cl and quinone.

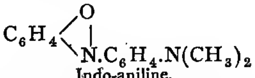
Quinone-dichlorimide, $C_6H_4(N_2Cl_2)$, from paraphenylenediamine-hydrochloride, crystallizes in needles which deflagrate at 124°, and are converted by reducing agents into *p*-phenylene-diamine.

Dibrom-quinone-chlorimide, $C_6Br_2H_2(ONCl)$, from dibrom-*p* nitro-phenol, crystallizes in dark yellow prisms, melting at 80° and decomposing at 121°. **Trichlor-quinone-chlorimide**, $C_6Cl_3H(ONCl)$, from trichlor-*p*-amidophenol, forms yellow prisms, melting at 118°.

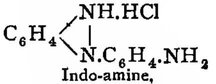
Indophenols, *Indoanilines* and *Indoamines*.—These are green to blue-colored dye-substances. In constitution they are analogous to the quinone-chlorimides and quinone-dichlorimides; they bear a close genetic relation to the latter, and are obtained by allowing the quinone-chlorimides and -dichlorimides to act upon phenols and anilines:—



Indo-phenol,
Quinone-phenolimide.

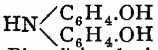


Indo-aniline,
Quinone-dimethyl-anilinimide.



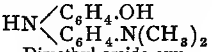
Indo-amine,
Phenylene Blue.

These compounds also contain the chromophore groups O—N and N—N (see p. 644), which occupy the para-position in one benzene nucleus; they are also closely related to the thionine dyestuffs (p. 605). They are decolorized upon reduction (the addition of 2H-atoms) which is true of most coloring compounds. By this action the chromophore group is severed, and derivatives of diphenylamine are formed, which are their leuco-compounds (p. 605). Thus, by reducing (dibrom) quinone-phenolimide we obtain (dibrom) *p*-dioxydiphenylamine (p. 604), and the same treatment converts indoaniline into dimethylamido-oxy-diphenylamine, and phenylene blue into *p*-diamido-diphenylamine (p. 603):—



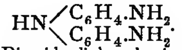
$HN{<}\begin{matrix}C_6H_4.OH\\ C_6H_4.OH\end{matrix}$

p-Dioxydiphenylamine.



$HN{<}\begin{matrix}C_6H_4.OH\\ C_6H_4.N(CH_3)_2\end{matrix}$

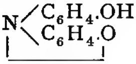
Dimethyl-amido-oxy-diphenylamine.



$HN{<}\begin{matrix}C_6H_4.NH_2\\ C_6H_4.NH_2\end{matrix}.$

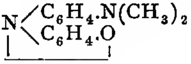
Diamido-diphenylamine.

Therefore, the indophenols, indoanilines and indoamines may be viewed as *derivatives of diphenylamine*, in accordance with the following formulas of like significance as those above (Nietzki, *Berichte*, 21, 1736):—



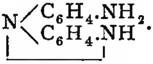
$N{<}\begin{matrix}C_6H_4.OH\\ C_6H_4.O\end{matrix}$

Indophenol.



$N{<}\begin{matrix}C_6H_4.N(CH_3)_2\\ C_6H_4.O\end{matrix}$

Indoaniline.

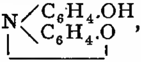
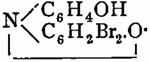


$N{<}\begin{matrix}C_6H_4.NH_2\\ C_6H_4.NH\end{matrix}.$

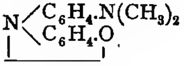
Indoamine.

The connection of the three groups is evident from the fact that the indoamines, by the replacement of the amido-group by oxygen, can be converted into indoanilines, and the latter, furthermore, into indophenols (Möhlau, *Berichte*, 16, 2843, and 18, 2915).

(1) The indophenols, in addition to their formation from the action of quinone chlorimide upon phenol, are also produced by oxidizing a mixture of a para-amido phenol and phenol (1 molecule of each). They dissolve in alcohol with a red color, and possess a phenol-like character. Their salts with the alkalies and ammonia dissolve in water with a *blue* color.

Quinone-phenol-imide,  $N{<}\begin{matrix}C_6H_4.OH\\ C_6H_4.O\end{matrix}$, also results upon heating phenol-blue with soda-lye (*Berichte*, 18, 2916), but owing to its instability, cannot be obtained in a free condition. **Dibrom-quinone-phenolimide,**  $N{<}\begin{matrix}C_6H_4OH\\ C_6H_2Br_2.O\end{matrix}.$ Its sodium salt is produced by the action of dibromquinone-chlorimide in alcoholic solution upon an alkaline phenol solution. It separates in golden green crystals, which dissolve in water with a blue color. Free dibrom-phenolimide, separated from its sodium salt by acetic acid, crystallizes in dark red prisms having a metallic lustre; they dissolve in alcohol and ether with a fuchsine-red color. Strong mineral acids decompose it into dibromphenol and quinone.

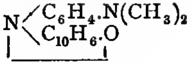
(2) **The Indo-anilines** (indophenols of Witt), as



$$N\begin{cases}C_6H_4.N(CH_3)_2\\C_6H_4.O\end{cases}$$

Phenol Blue.

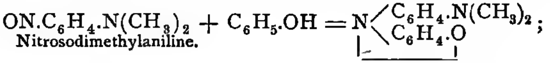
and



$$N\begin{cases}C_6H_4.N(CH_3)_2\\C_{10}H_6.O\end{cases}$$

Naphthol Blue.

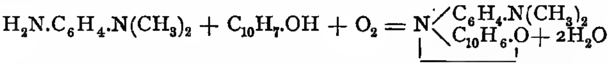
are produced: (1) by the action of quinone chlorimide upon dimethylaniline in alcoholic solution (see above); (2) by the action of nitroso- and nitro-dimethylaniline upon phenol and α-naphthol in alkaline solution, especially in the presence of reducing agents (Witt, 1879):—



$$\underset{\text{Nitrosodimethylaniline.}}{ON.C_6H_4.N(CH_3)_2} + C_6H_5.OH = N\begin{cases}C_6H_4.N(CH_3)_2\\C_6H_4.O\end{cases};$$

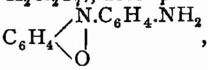
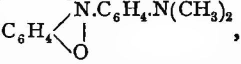
Phenol Blue.

(3) By the oxidation in *alkaline* solution (with sodium hypochlorite), of a mixture of a para-phenylene diamine with a phenol, or of a para-amido-phenol with a primary monamine; this is the readiest method for its preparation. Thus there is formed from dimethyl-*p*-phenylene diamine (p. 625) with α-naphthol, the so-called *naphthol blue*:—

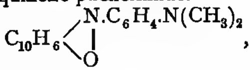


$$H_2N.C_6H_4.N(CH_3)_2 + C_{10}H_7.OH + O_2 = N\begin{cases}C_6H_4.N(CH_3)_2\\C_{10}H_6.O\end{cases} + 2H_2O.$$

Naphthol Blue.

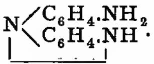
The indoanilines, in distinction to the indophenols, are feebly *basic*, and are not capable of forming salts with alkalies. They are rather stable towards the latter; acids quickly decompose them into quinones and the *p*-phenylene diamines. They are changed to the leuco-compounds by reduction (absorption of two hydrogen atoms); these dissolve readily in alkalies, and are readily reconverted (oxidized) into indoanilines (by exposure of their alkaline solution to the air). The free indoanilines have a deep-blue color, and can be applied as dyestuffs. For this purpose they are converted into their alkaline leuco-derivatives, which are soluble, and the material is impregnated or printed with these. Oxidation (by exposure to the air, or with $K_2Cr_2O_7$), develops the color. The simplest aniline is **Quinone Anilinimide,**  $C_6H_4\begin{cases}N.C_6H_4.NH_2\\O\end{cases}$, a violet dye, formed by the oxidation of *p*-phenylene diamine, $C_6H_4(NH_2)_2$, with phenol. Its dimethyl derivative is **Quinone-dimethyl-anilinimide,**  $C_6H_4\begin{cases}N.C_6H_4.N(CH_3)_2\\O\end{cases}$,

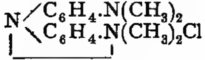
Phenol Blue. This results from dimethyl-*p*-phenylene diamine and phenol. It has a greenish-blue color. When boiled with soda-lye it splits off dimethylamine and becomes quinone phenolimide.

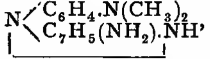
Naphthol Blue,  $C_{10}H_6\begin{cases}N.C_6H_4.N(CH_3)_2\\O\end{cases}$, called *indophenol* (Koechlin and Witt), finds technical application. It is made by oxidizing dimethyl-*p*-phenylene diamine with α-naphthol (*Berichte*, 18, 2916), or by the action of nitrosodimethylaniline upon α-naphthol. It crystallizes from alcohol in bronze-like, bluish violet crystals, dissolves without coloration in acids, and on standing in contact with the same decomposes into dimethyl-*p*-phenylene diamine and α-naphthoquinone. When reduced with $SnCl_2$, it yields the $SnCl_2$-double salt, which occurs in commerce as a paste, bearing the name "white indophenol."

(3) Indamines (see above).

These arise by oxidation, in neutral solution and in the cold, of a mixture of a *p*-phenylene diamine with an aniline (Nietzki), or by the action of nitrosodimethyl aniline upon anilines or *m*-diamines (Witt). They are feeble bases, forming blue or green-colored salts with acids, but with an excess of the latter are very easily split up into quinone and the diamine. Because of their instability they find no application, and are only important as intermediate products in the manufacture of safranine dyestuffs (into which they can be readily transposed) (*Berichte*, 16, 464). The simplest indamine is—

Phenylene Blue, $C_{12}H_{11}N_3$ =  $N\left\langle\begin{matrix}C_6H_4.NH_2\\C_6H_4.NH\end{matrix}\right.$. This is produced by the oxidation of *p*-phenylene diamine with aniline. Its salts are greenish-blue in color. It yields diamido-diphenylamine by reduction. Its tetramethyl-derivative is—

Dimethylphenylene Green, $C_{16}H_{19}N_3.HCl$ =  $N\left\langle\begin{matrix}C_6H_4.N(CH_3)_2\\C_6H_4.N(CH_3)_2Cl\end{matrix}\right.$ (Bindschedler's green). This is obtained by oxidizing dimethyl paraphenylene diamine with dimethyl aniline. Its salts dissolve in water with a beautiful green color, and impart a yellow-green color to silk. Its reduction yields tetramethyl-diamido-diphenylamine (p. 604). Digestion with dilute acids resolves it into quinone and dimethylamine (*Berichte*, 16, 865). When it is boiled with soda-lye, dimethylamine splits off and phenol blue is produced; this further separates into quinone phenolimide (p. 706) (*Berichte*, 18, 2915).

Toluylene Blue, $C_{15}H_{18}N_4$ =  $N\left\langle\begin{matrix}C_6H_4.N(CH_3)_2\\C_7H_5(NH_2).NH\end{matrix}\right.$, results from ordinary toluylene diamine (p. 626) by oxidizing it mixed with dimethyl-*p*-phenylene diamine, or by the action of HCl-nitroso-dimethylaniline. Its salts with one equivalent of acid are of a beautiful blue color, and are decolorized by an excess of mineral acids with formation of the diacid salts. It is converted into toluylene red (see this) on boiling with water.

The lowest homologue of toluylene blue is produced by reducing dimethylamido-dinitro-diphenylamine (p. 604), and oxidizing the resulting triamido-compound (*Berichte*, 23, 2738).

ALCOHOLS.

The *true alcohols* (isomeric with the phenols) of the benzene series are produced by the entrance of hydroxyls into the side-chains of the homologous benzenes (p. 557). They are perfectly analogous to the fatty alcohols. By oxidation they yield aldehydes (or ketones) and acids:—

$C_6H_5.CH_2.OH$	$C_8H_5.CHO$	$C_6H_5.CO.OH.$
Benzyl Alcohol.	Benzaldehyde.	Benzoic Acid.

The methods of forming them are perfectly analogous to those of the fatty series. They are obtained:—

1. By the conversion of substituted hydrocarbons, like benzyl chloride, $C_6H_5.CH_2Cl$, into acid esters, and saponifying the latter with alkalies, or by boiling the chlorides with water and lead oxide (p. 119), or with a soda solution:—

$$\underset{\text{Benzyl Chloride.}}{C_6H_5.CH_2Cl} + H_2O = \underset{\text{Benzyl Alcohol.}}{C_6H_6.CH_2.OH} + HCl.$$

2. By the action of nascent hydrogen (p. 119) on the aldehydes and ketones, or by heating the aldehydes, or letting them stand with alcoholic or aqueous potash, whereby acids are formed at the same time:—

$$2C_6H_5.CHO + KOH = C_6H_5.CH_2.OH + C_6H_5.CO_2K.$$

In this series we also distinguish *primary*, *secondary* and *tertiary* alcohols.

Benzyl Alcohol, $C_7H_8O = C_6H_5.CH_2.OH$, occurs as benzyl-benzoic ester, and benzyl-cinnamic ester in the balsams of Peru and Tolu, and in storax, and can be obtained from benzaldehyde (oil of bitter almonds) by the action of sodium amalgam or aqueous potassium hydroxide (*Berichte*, 14, 2394), or by boiling benzyl chloride with a soda solution. It is a colorless liquid, with a faint aromatic odor, and boils at 206°; its specific gravity at 0° is 1.062. It dissolves with difficulty in water, but readily in alcohol and ether. It yields benzaldehyde and benzoic acid when oxidized. Heated with hydrochloric acid or hydrobromic acid, the OH-group is replaced by halogens. Benzoic acid and toluene result on distilling it with concentrated potash:—

$$3C_7H_8O + KOH = C_7H_5KO_2 + 2C_7H_8 + 2H_2O.$$

The *esters* of benzyl alcohol are produced from it by the action of acid chlorides, or from benzyl chloride by boiling with organic salts. The *acetic ester*, $C_7H_7O.C_2H_3O$, is a liquid and boils at 206°. The *oxalic ester*, $C_2O_4(C_7H_7)_2$, forms shining leaflets, melting at 80°.

The *alcohol ethers* are obtained by heating benzyl chloride with sodium alcoholates. The *methyl ether*, $C_7H_7O.CH_3$, boils at 168°; the *ethyl ether* at 185°.

The *dibenzyl ether*, $(C_6H_5.CH_2)_2O$, is formed on heating the alcohol with boric anhydride, and benzyl chloride with water to 190°. It is an oil boiling near 310°.

The *benzyl-phenyl ether*, $C_6H_5.CH_2.O.C_6H_5$, results when benzyl chloride is heated together with potassium phenolate, $C_6H_5.OK$. It melts at 39°, and boils at 287°.

Substituted benzyl alcohols are derived from substituted benzyl chlorides, *e. g.*, $C_6H_4Cl.CH_2Cl$, when they are heated with aqueous ammonia, or by means of acetic esters. **Para-chlor-benzyl alcohol**, $C_6H_4Cl.CH_2.OH$, consists of long needles, which melt at 66°, and boil about 220°.

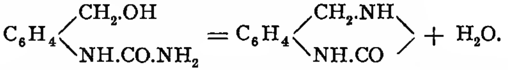
o-**Nitrobenzyl Alcohol**, $C_6H_4(NO_2).CH_2.OH$, is formed by shaking *o*-nitrobenzaldehyde (crude) with concentrated sodium hydroxide (*Berichte*, 18, 2403), and crystallizes in bright yellow needles, melting at 74°. *m*-**Nitrobenzyl Alcohol**, from *m*-nitrobenzaldehyde, is a thick, yellow oil.

p-**Nitrobenzyl Alcohol** is obtained from its chloride and from nitrobenzyl acetic ester. It melts at 93°.

Nitromethyl Benzene, $C_6H_5.CH_2(NO_2)$, is obtained from nitrobenzalphthalide; it is a yellow-colored liquid, boiling at 226° (*Berichte*, 18, 1255; 19, 1145).

o **Amidobenzyl Alcohol**, $C_6H_4(NH_2).CH_2.OH$, is formed by the reduction of anthranil and *o*-nitrobenzyl alcohol with zinc dust and hydrochloric acid. It crystallizes in white needles, has an aniline odor, and melts at 82° (*Berichte*, 15, 2109). Benzylenimide,  $C_6H_4\left\langle\begin{matrix}NH_2\\CH_2\end{matrix}\right\rangle$?, is the anhydride of this alcohol. It results from the reduction of *o*-nitrobenzyl chloride with stannous chloride. An analogous compound is also obtained from *p*-nitrobenzyl chloride (*Berichte*, 19, 1612).

Potassium cyanate converts *o*-amidobenzyl alcohol into a urea, that condenses to a benzo-metadiazine (*Berichte*, 23, 2183):—



$$C_6H_4\left\langle\begin{matrix}CH_2.OH\\NH.CO.NH_2\end{matrix}\right. = C_6H_4\left\langle\begin{matrix}CH_2.NH\\NH.CO\end{matrix}\right\rangle + H_2O.$$

Benzyl Sulphydrate, $C_6H_5.CH_2.SH$, Benzyl Mercaptan. This is formed by the action of alcoholic KSH upon benzyl chloride. It is a liquid, with a leek-like odor; boils at 194°, and at 20° has a specific gravity = 1.058. Salts of the heavy metals precipitate mercaptides from its alcoholic solutions. On exposure it oxidizes to **Benzyl disulphide,** $(C_7H_7)_2S_2$, which crystallizes from alcohol in shining leaflets melting at 66°. Nascent hydrogen causes it to revert to benzyl sulphydrate.

Benzyl Sulphide, $(C_6H_5.CH_2)_2S$, is formed by the action of K_2S upon an alcoholic solution of benzyl chloride. Colorless needles, melting at 49°. Nitric acid oxidizes it to the oxy-sulphide, $(C_6H_5.CH_2)_2SO$, which dissolves in hot water and melts at 130°. The *sulphone*, $(C_6H_5.CH_2)_2SO_2$, melts at 150°.

Potassium Benzylsulphonate, $C_6H_5.CH_2.SO_3K + H_2O$, is formed on boiling benzyl chloride with potassium sulphite. The free acid is a deliquescent crystalline mass; it is isomeric with toluene-sulphonic acid.

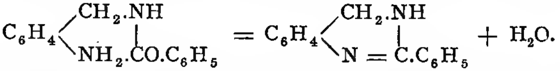
Alcoholic ammonia converts benzyl chloride into mono-, di-, and tri-benzylamines, which are separated by means of their hydrochloric acid salts. These same compounds are obtained from benzaldehyde on boiling with formamide (*Berichte*, 19, 2128; 20, 104). They result, too, when the benzothio-amides are reduced with zinc and hydrochloric acid:—

$$C_6H_5.CS.NH_2 + 2H_2 = C_6H_5.CH_2.NH_2 + SH_2.$$

(*Berichte*, 21, 51).

Benzylamine, $C_6H_5.CH_2.NH_2$ (Benzamine), is formed when zinc and hydrochloric acid act upon benzonitrile; by the action of an alkaline bromine solution upon phenylacetamide, $C_6H_5.CH_2.CO.NH_2$ (p. 160), but most readily by decomposing benzylacetamide, $C_6H_5.CH_2.NH.CO.CH_3$ (from benzyl chloride with acetamide, *Berichte*, 19, 1286), by means of alcoholic potash. It dissolves in water and boils at 185°. It differs from its isomeric toluidine in being a strong base, that attracts carbon dioxide.

o-**Nitrobenzylamine,** $C_6H_4(NO_2).CH_2.NH_2$, obtained from *o*-nitrobenzylchloride (p. 584) by the saponification of its phthalimide derivative, is a strong, oily base (*Berichte*, 20, 2228). It may be reduced to *o*-**amido-benzylamine,** $C_6H_4(NH_2).CH_2.NH_2$ (*o*-benzylene-diamine). The benzene derivative of the latter forms a quinazoline by the production of a closed ring (*Berichte*, 23, 2810):—



$$C_6H_4\left\langle\begin{matrix}CH_2.NH\\ \quad\ \ |\\NH_2.CO.C_6H_5\end{matrix}\right. = C_6H_4\left\langle\begin{matrix}CH_2.NH\\ \qquad |\\N = C.C_6H_5\end{matrix}\right. + H_2O.$$

Dibenzylamine, $(C_7H_7)_2.NH$, is an oil insoluble in water. It is formed when PCl_3 acts upon dibenzylhydroxylamine (*Berichte* 19, 3287).

Tribenzylamine, $(C_7H_7)_3N$, forms large plates melting at 91°, and distilling near 300° undecomposed (*Berichte*, 19, 1027).

When benzyl chloride acts on aniline the products are:—

Benzylaniline, $C_6H_5.CH_2.NH.C_6H_5$, which also results in the reduction of benzylidene aniline with sodium in alcoholic solution. It melts at 32°, and

Dibenzylaniline, $(C_6H_5.CH_2)_2.N.C_6H_5$, melting at 67°.

Benzyl derivatives of hydroxylamine (p. 166) (*Annalen*, 257, 203).

α-Benzyl-hydroxylamine, $H_2N.O.C_7H_7$, is produced by decomposing acetoxime-benzyl ether (p. 205) and α-benzaldoximebenzyl ether with hydrochloric acid. It is a colorless oil, boiling at 119° under 30 mm. pressure. Its hydrochloride forms silvery leaflets, subliming above 230° without previously melting. If it be heated with hydrochloric acid it breaks down into benzyl chloride, hydroxylamine and ammonium chloride. Hydriodic acid converts it into benzyl iodide and ammonia.

β-Benzyl-hydroxylamine, $C_7H_7.HN.OH$, is obtained by decomposing β-benzaldoximebenzyl ether (p. 718) and αβ-dibenzyl-hydroxylamine with hydrochloric acid. It melts at 57°, dissolves somewhat in water, and *reduces* Fehling's solution. Its hydrochloride is very readily soluble in water and alcohol. It melts at 100–110° (*Berichte*, 22, 429, 613). Hydrochloric acid does not decompose it. It yields bimolecular benzaldoxime (*Berichte*, 23, 1773) by oxidation.

αβ-Dibenzyl-hydroxylamine, $C_7H_7.HN.O.C_7H_7$, results upon heating α-benzyl-hydroxylamine with benzyl chloride. It is a liquid. A large quantity of water will decompose its hydrochloride. It becomes β-benzyl-hydroxylamine by decomposition.

ββ-Dibenzyl-hydroxylamine, $(C_7H_7)_2N.OH$, is produced on heating hydroxylamine with benzyl chloride. It melts at 123°. Hydrochloric acid does not decompose it.

Tribenzyl-hydroxylamine, $(C_7H_7)_2N.O.C_7H_7$, results when benzyl chloride acts upon αβ-dibenzyl-hydroxylamine (less readily if the ββ-variety be used). It is a liquid. Its hydrochloride is readily decomposed by water. With hydrochloric acid it yields ββ-dibenzyl-hydroxylamine (*Berichte*, 23, Ref. 402).

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(2) Alcohols, $C_8H_{10}O$. There are five isomerides.

Tolyl Alcohols, $C_6H_4(CH_3).CH_2.OH$. The *ortho*-body (1, 2). obtained from orthotoluyl aldehyde with sodium amalgam, melts at 31°, and boils at 210°. (*Berichte*, 23, 1028). The *meta*, from *m*-xylene bromide, $C_6H_4(CH_3).CH_2Cl$, boils at 217° (*Berichte*, 18, Ref. 66). The *para*, derived from paratoluyl aldehyde with potassium hydroxide, melts at 59°, and boils at 217°.

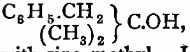
Phenyl Ethyl Alcohol, $C_6H_5.CH_2.CH_2.OH$, α-Tolyl alcohol, obtained from α-toluyl aldehyde, is a liquid boiling at 212°, has a specific gravity = 1.033 at 20°, and when moderately oxidized yields α-toluic acid. Its acetic ester boils at 224°. See *Berichte*, 22, 1413 for the phenylethylamines, $C_6H_5.C_2H_4.NH_2$.

Phenyl Methyl Carbinol, $C_6H_5.CH(OH).CH_3$, is a secondary alcohol, produced from β-brom-ethyl benzene (p. 586), and by the action of sodium amalgam upon acetophenone, $C_6H_5.CO.CH_3$. It boils at 203°. Oxidation converts it again into acetophenone. The acetic ester boils near 214°, and partly decomposes into acetic acid and styrol.

(3) **Phenyl Propyl Alcohol**, $C_6H_5.CH_2.CH_2.CH_2(OH)$, Hydrocinnamyl Alcohol, obtained from cinnamic alcohol, boils at 235°. It exists as cinnamic ester in storax. Secondary **Phenyl-ethyl Carbinol**, $C_6H_5.CH(OH).CH_2.CH_3$, is formed from phenyl-ethyl ketone, $C_6H_5.CO.C_2H_5$, and boils at 219°.

(4) **Cumin Alcohol**, $C_6H_4\left\langle\begin{array}{l}C_3H_7\\CH_2.OH\end{array}\right.$ (1, 4), contains the isopropyl-group.

It is formed from cuminic aldehyde. It boils at 246°, and yields common cymene, $C_{10}H_{14}$, when boiled with zinc dust. Its chloride, $C_6H_4(C_3H_7).CH_2Cl$, yields the same product, when heated with zinc and hydrochloric acid. Boiling alcoholic potash or dilute nitric acid oxidizes it to cuminic acid. Its isomeride is tertiary—

Benzyl-dimethyl Carbinol,  $\left.\begin{matrix}C_6H_5.CH_2\\(CH_3)_2\end{matrix}\right\}C.OH$, produced by acting on *a*-toluic chloride, $C_6H_5.CH_2.COCl$, with zinc methyl. Long needles, which melt at 20–22°, and boil about 225°.

DIVALENT (DIHYDRIC) ALCOHOLS.

Dihydric *Benzylene-Glycol*, $C_6H_5.CH(OH)_2$, would correspond to methylene glycol, but does not exist. Where it should occur, benzaldehyde appears (p. 298). Its ethers are derived from benzylene chloride, $C_6H_5.CHCl_2$, through the action of sodium alcoholates or salts of organic acids. The *dimethyl ether*, $C_6H_5.CH(O.CH_3)_2$, boils at 205°; the *diethyl ether* at 217°. The *acetate*, $C_6H_5.CH(O.C_2H_3O)_2$, is crystalline, melts at 43°, and boils with decomposition at 220°.

Tollylene Alcohols, $C_8H_{10}O_2$ =  $C_6H_4\begin{matrix}\diagup CH_2.OH\\\diagdown CH_2.OH\end{matrix}$, Xylylene alcohols. The three isomerides are obtained from the three corresponding xylylene chlorides or bromides by boiling with a soda solution. The *ortho* (1, 2), called **Phthalyl alcohol,** is obtained also from phthalic acid chloride by sodium amalgam. It melts at 64°. A potassium permanganate solution oxidizes it to phthalic acid. The *meta* (1, 3) melts at 46°, while the *para* melts at 112°. The three are readily soluble in water.

Styrolene Alcohol, $C_6H_5.CH(OH).CH_2.OH$, Phenyl glycol, is obtained from styrolene dibromide, $C_6H_5.CHBr.CH_2Br$; it crystallizes from benzine, and benzene, in silky needles, melts at 67–68°, and can be sublimed. It is very soluble in water, alcohol and ether. Dilute nitric acid oxidizes it to benzoyl carbinol.

Phenyl Methyl Glycol, $C_6H_5.CH(OH).CH(OH).CH_3$, exists in two modifications, *a* and *β*, like hydrobenzoïn. These are obtained from phenyl dibrompropane, $C_6H_5.CHBr.CHBr\,CH_3$ (from propyl benzene). The *a*-body melts at 53°, the *β*- at 93° (*Berichte*, 17, 709).

Benzoyl Carbinol, $C_6H_5.CO.CH_2.OH$ (Acetophenone Alcohol), is a *Ketone* alcohol, formed from the bromide, $C_6H_5.CO.CH_2.Br$, by its conversion into acetate, and saponification with potassium carbonate (*Berichte*, 16, 1290). It crystallizes from water and alcohol in large, brilliant leaflets, which contain water of crystallization, and melt at 73–74°. It crystallizes from ether in shining anhydrous plates, and melts at 85–86°.

When distilled it decomposes with formation of bitter almond oil. Being a ketone it forms crystalline compounds with primary alkaline sulphites. Like acetyl carbinol it reduces a cold ammoniacal silver or copper solution (forming benzaldehyde and benzoic acid), and is oxidized to mandelic acid (p. 321 *Berichte*, 14, 2100). Nitric acid oxidizes it to benzoyl-carboxylic acid, $C_6H_5.CO.CO_2H$. It yields cyanhydrin with CNH, which then forms *a*-phenyl glyceric acid. Hydroxylamine converts it into the isonitroso-compound, $C_6H_5.C(N.OH).CH_2.OH$, melting at 70°.

It forms the hydrazone, $C_6H_5.C(N_2H.C_6H_5).CH_2OH$ (melting at 112°), with phenylhydrazine. This compound unites with a second molecule of the reagent, like the glucoses (p. 501), and yields the *osazone*, $C_6H_5.C(N_2H.C_6H_5)CH(N_2H.C_6H_5)$ (*Berichte*, 20, 822).

The *acetate*, $C_6H_5.CO.CH_2.O.C_2H_3O$, forms rhombic plates, melting at 49°; the *benzoate* melts at 117°; both reduce an ammoniacal silver solution, even in the cold.

Oxy-alcohols or Phenol alcohols.

These contain, in addition to the alcoholic hydroxyl, one or more hydroxyl groups in combination with the benzene nucleus, hence they also possess the properties of the phenols.

(1) Oxy-benzyl alcohols, 

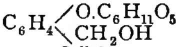
$C_6H_4\left\langle\begin{array}{l}OH\\CH_2.OH.\end{array}\right.$

The ortho-compound (1, 2), **Saligenin**, is formed when sodium amalgam acts upon salicylic aldehyde, or in the decomposition of the glucoside salicin with dilute acids or ferments:—

$$\underset{\text{Salicin.}}{C_{13}H_{18}O_7} + H_2O = \underset{\text{Saligenin.}}{C_7H_8O_2} + \underset{\text{Dextrose.}}{C_6H_{12}O_6}.$$

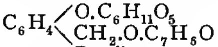
It consists of pearly tables, soluble in hot water, alcohol and ether, melting at 82° and subliming near 100°. Lead acetate causes a white precipitate in its solutions, and ferric chloride produces a deep blue color in them. Dilute acids resinify it, forming *saliretin*, $C_{14}H_{14}O_3$. It yields salicylic acid when oxidized.

The glucosides of saligenin are *salicin*, *populin* and *helicin* :—



$C_6H_4\left\langle\begin{array}{l}O.C_6H_{11}O_5\\CH_2OH\end{array}\right.$

Salicin.



$C_6H_4\left\langle\begin{array}{l}O.C_6H_{11}O_5\\CH_2.O.C_7H_5O\end{array}\right.$

Populin.

$C_6H_4\left\langle\begin{array}{l}O.C_6H_{11}O_5\\CHO\end{array}\right.$

Helicin.

Salicin, $C_{13}H_{18}O_7$, the glucoside of saligenin, occurs in the bark and leaves of willows and some poplars, from which it may be extracted with water. It can be artificially prepared by reducing helicin with sodium amalgam. It forms shining crystals, which dissolve easily in hot water and alcohol, and melt at 198°. Its taste is bitter.

The glucoside, *Populin*, $C_{20}H_{22}O_8$, contained in several varieties of poplar, is the benzoyl derivative of salicin, $C_{13}H_{17}(C_7H_5O)O_7$, and can be artificially made by the action of benzoyl chloride, C_7H_5OCl, or benzoic anhydride upon salicin. Populin crystallizes in small prisms containing 2 molecules of water, dissolves with difficulty in water and possesses a sweet taste. Dilute hydrochloric acid decomposes it into benzoic acid, glucose and saliretin.

Helicin, $C_6H_4(O.C_6H_{11}O_5).CHO$, is produced by oxidizing salicin with nitric acid. It can be artificially prepared from salicylic aldehyde and acetochlorhydrose. It dissolves with difficulty in water, crystallizes in small needles and melts at 175°. Dilute acids and ferments break it up into salicylic aldehyde and dextrose. It contains the CHO-group, hence combines with acetaldehyde to form glucose-cumaraldehyde, $C_6H_4(O.C_6H_{11}O_5).CH:CH.CHO$ (*Berichte*, 18, 1958).

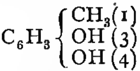
Meta-oxybenzyl Alcohol, $C_6H_4(OH).CH_2.OH$ (1, 3), is formed from meta-oxybenzoic acid by means of sodium amalgam. It melts at 67°, and boils at 300°.

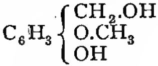
Ferric chloride colors it violet. It is oxidized to meta-oxybenzoic acid when fused with KOH (but not with chromic acid, p. 686).

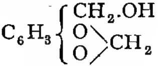
Para-oxybenzyl Alcohol (1, 4) is produced by the action of sodium amalgam (in slightly acidulated alcoholic solution) upon paraoxybenzaldehyde (dioxy-hydrobenzoïn, melting at 222°, is produced at the same time). It is readily soluble in water, alcohol and ether. From benzene it crystallizes in delicate needles, melting at 110° (*Berichte*, 19, 2374). It melts at 197°. Its methyl ether is the so-called

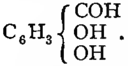
Anisyl Alcohol, $C_6H_4(O.CH_3).CH_2.OH$ (1, 4), obtained from anisic aldehyde by alcoholic potassium hydroxide. It is but slightly soluble in water, crystallizes in needles, melts at 25°, and boils at 259° without decomposition. It forms anisic aldehyde and acid when oxidized.

(2) **Vanillin Alcohol,** $C_8H_{10}O_3$, and **Piperonyl Alcohol,** $C_8H_8O_3$, are formed from their aldehydes, vanillin and piperonal, by acting on the solution with sodium amalgam. They are derivatives of homo-pyro-catechin and creosol (p. 693), and stand in intimate relation to proto-catechuic aldehyde. Vanillin alcohol is the methyl-phenol ether, piperonyl alcohol the methylene-phenol ether of protocatechuic alcohol, which has not yet been prepared (see vanillin):—


$$C_6H_3\begin{cases}CH_3(1)\\OH\ (3)\\OH\ (4)\end{cases}$$
Homo-pyro-catechin.


$$C_6H_3\begin{cases}CH_2.OH\\O.CH_3\\OH\end{cases}$$
Vanillin Alcohol.


$$C_6H_3\begin{cases}CH_2.OH\\ \left.\begin{array}{l}O\\O\end{array}\right>CH_2\end{cases}$$
Piperonyl Alcohol.


$$C_6H_3\begin{cases}COH\\OH\\OH\end{cases}.$$
Protocatechuic Aldehyde.

Vanillin alcohol crystallizes in colorless prisms, melts at 115°, and dissolves easily in hot water and alcohol. Piperonyl alcohol dissolves with difficulty in water, forms long prisms, and melts at 51°.

TRIHYDRIC ALCOHOLS.

Phenyl Glycerol (Stycerine), $C_9H_{12}O_3 = C_6H_5.CH(OH).CH(OH).CH_2.OH$, is obtained from the bromide of cinnamic alcohol, $C_6H_5.CHBr.CHBr.CH_2.OH$, by long boiling with water. It is a gummy mass, easily soluble in water and alcohol.

Mesitylene Glycerol, $C_6H_3(CH_2.OH)_3$, Mesicerine, is produced from tribrom-mesitylene, $C_6H_3(CH_2Br)_3$ (melting at 94°), upon boiling with water and lead carbonate. It is a thick liquid.

ALDEHYDES.

The aldehydes of the benzene series, characterized by the group CHO, are perfectly analogous, as regards methods of formation and properties, with slight modifications, to those of the paraffin series. They are distinguished as *monovalent* aldehydes, like:

$C_6H_5.CHO$	$C_6H_5.CH_2.CHO$	$C_6H_4(CH_3)CHO$, etc.
Benzaldehyde.	Phenyl-acetaldehyde.	Tolylaldehyde.

and divalent or *dialdehydes*, like phthalic aldehyde, $C_6H_4(CHO)_2$. Aldehydes of mixed function also occur, *e. g.*, *aldehydephenols* or *oxyaldehydes*, $C_6H_4(OH).CHO$, etc.

The monovalent aldehydes are obtained by the oxidation of the corresponding primary alcohols, or by the distillation of the calcium salts of the aromatic acids with calcium formate (p. 187). They are derived from the benzene homologues by heating the halogen derivatives, $C_6H_5.CHCl_2$, with water, especially in the presence of bases (like sodium carbonate, lime or lead oxide), or by boiling the mono-chlor-derivatives, $C_6H_5.CH_2Cl$, with water, in presence of oxidizing agents (lead nitrate).

A very interesting and direct conversion of homologous benzenes into aldehydes, is that occurring in the action of chromyl chloride, CrO_2Cl_2, and water (Etard).

Here the benzene homologues first unite (in CS_2-solution) with two molecules of chromyl chloride, forming brown pulverulent double compounds, *e. g.*, $C_6H_5.CH_3.(CrO_2Cl_2)_2$, which yield aldehydes when added to water (*Berichte*, 17, 1462 and 1700). All the alkylic benzenes sustain this transformation; thus, from toluene, $C_6H_5.CH_3$, we obtain benzaldehyde, $C_6H_5.CHO$. The xylenes yield tolylaldehydes, and the *o*-haloid toluenes, yield the *o*-haloid benzaldehydes (*Berichte*, 21, Ref. 714). With benzenes, containing higher alkyls, the reaction is more complicated, as ketones are also produced, thus: propyl benzene, $C_6H_5.C_3H_7$, yields benzylmethyl ketone, $C_6H_5.CH_2.CO.CH_3$ (*Berichte*, 23, 1070).

The benzaldehydes are mostly liquid bodies, which dissolve with difficulty in water, possess an aromatic odor, and in deportment are very similar to the fatty aldehydes. They do not reduce alkaline copper (p. 189), but do reduce silver solutions with the production of a metallic mirror. They differ from the fatty aldehydes in that they are, as a general thing, readily oxidized to alcohols and acids by alcoholic or aqueous alkalies (p. 708); it appears that this reaction is, however, only peculiar to those aldehydes in which the CHO-group is in direct union with the benzene nucleus. Furthermore, they do not directly combine with ammonia (p. 189), the amines and hydrazines, but yield compounds with them with immediate separation of water, and in the new derivatives all the amide hydrogen is replaced by the aldehyde radicals:—

$$3C_6H_5.CHO + 2NH_3 = \underset{\text{Hydrobenzamide.}}{(C_6H_5.CH)_3N_2} + 3H_2O,$$

$$C_6H_5.CHO + H_2N.C_6H_5 = \underset{\text{Benzylidene-Aniline.}}{C_6H_5.CH{:}N.C_6H_5} + H_2O.$$

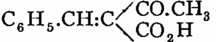
Alcoholic potassium cyanide converts the benzaldehydes into benzoins (see these). Again, the benzaldehydes, like all benzene derivatives, readily furnish substitution products. An interesting fact is their ability to afford condensation products with the most heterogeneous bodies, water always disappearing (p. 194).

Thus, by condensation with the acids, aldehydes and ketones of the fatty series, we obtain unsaturated acids, aldehydes and ketones, *e.g.*:—

$C_6H_5.CH:CH.CO_2H$	$C_6H_5.CH:CH.CHO$	$C_6H_5.CH:CH.CO.CH_3$.
Cinnamic Acid.	Cinnamic Aldehyde.	Benzylidene Acetone.

Occasionally an aldol condensation occurs here (p. 195), with formation of oxy-bodies, *e.g.*, $C_6H_5.CH.(OH).CH_2.CO_2H$, phenyl lactic acid, which give off water in addition. Such a condensation follows in consequence of the action of HCl-gas, zinc chloride, sulphuric acid and glacial acetic acid (*Berichte*, 14, 2460), or upon heating with acetic anhydride. The condensing influence (especially with acetone and acetaldehyde) of aqueous alkalies, *e.g.*, dilute sodium hydroxide and baryta water (*Berichte*, 14, 2468, and 16, 2205), is particularly interesting.

With very dilute aqueous sodium hydroxide (2%) it is possible for an aldol condensation to occur here, whereas if the solution be alcoholic, with 10% sodium hydroxide, there is an immediate separation of water (*Berichte*, 18, 484, 720).

With malonic acid, the benzaldehydes form unsaturated dibasic acids, *e.g.*, benzal-malonic acid, $C_6H_5.CH:C(CO_2H)_2$, with acetacetic esters, acetyl carbonic acids, *e.g.*, benzal-acetacetic acid,  $C_6H_5.CH:C\begin{matrix}\diagup CO.CH_3\\ \diagdown CO_2H\end{matrix}$ (*Annalen*, 218, 121, and 223, 137). The benzaldehydes also condense with benzenes, phenols and anilines, forming derivatives of triphenyl methane $(C_6H_5)_3CH$ (see this).

MONOVALENT ALDEHYDES.

1. **Benzaldehyde,** $C_7H_6O = C_6H_5.CHO$, **Bitter Almond Oil,** results from the oxidation of benzyl alcohol, and by the distillation of calcium benzoate and formate. Formerly it was prepared exclusively from its glucoside amygdalin (see below). At present it is made on a large scale from benzal chloride, $C_6H_5.CHCl_2$, with sulphuric acid, or by heating it under pressure with milk of lime, or by boiling benzyl chloride with water and lead nitrate. It is applied in the manufacture of benzoic and cinnamic acids, for preparing malachite green and other coloring substances.

The bitter-almond oil, prepared from chlorinated toluene, invariably contains chlorine; for its purification it is advisable to change it to its sodium bisulphite compound and then fractionate. Officinal bitter-almond oil is obtained from amygdalin; it usually contains hydrocyanic acid, which can be removed by shaking it with lime and ferrous chloride.

Bitter-almond oil is a colorless liquid with a pleasant odor, and high refractive power, and boils at 179°; its specific gravity = 1.050 at 15°. It is soluble in 30 parts water, and is miscible with alcohol and ether. It shows all the reactions of the aldehydes; when oxidized (even in the air) it forms benzoic acid; by reduction (sodium amalgam) it passes into benzyl alcohol (together with hydrobenzoïn).

It forms crystalline compounds with the alkaline sulphites. CNH converts it into *Cyanhydrin*, $C_6H_5.CH(OH).CN$ (mandelic nitrile) (p. 347)—a yellow oil, which solidifies on cooling. PCl_5 converts it into benzal chloride, $C_6H_5.CHCl_2$ (p. 584). Benzaldehyde dissolves in fuming sulphuric acid to form a crystalline sulphonic acid, $C_6H_4(CHO).SO_3H$, which forms salts, that crystallize well (*Berichte*, 16, 150).

A glucoside of benzaldehyde is *Amygdalin*, $C_{20}H_{27}NO_{11}$, occurring in the bitter almonds and in various plants, especially in the kernels of Pomaceæ and Amygdalaceæ, and the leaves of the cherry laurel. To obtain it the bitter almonds are freed of oil by pressing, and then digested with boiling alcohol, the solution is concentrated and the fatty oil removed with ether. Amygdalin crystallizes from alcohol in white, shining leaflets; it tastes bitter, and dissolves readily in water and hot alcohol. It crystallizes from water in prisms, containing $3H_2O$. It yields a heptacetate when gently warmed with acetic anhydride. On boiling with dilute acids, or upon standing with water and *emulsin*, a ferment present in bitter almonds, amygdalin, is decomposed into oil of bitter almonds, dextrose and hydrocyanic acid:—

$$C_{20}H_{27}NO_{11} + 2H_2O = C_7H_6O + 2C_6H_{12}O_6 + CNH.$$

When amygdalin is boiled with alkalies, the nitrogen is evolved as ammonia and *amygdalic acid*, $C_{20}H_{28}O_{13}$, produced; this decomposes into mandelic acid and glucoses, when boiled with dilute acids.

Hydrogen sulphide converts benzaldehyde into three isomeric *thiobenzaldehydes* $(C_7H_6S)_4$ (p. 197) (*Berichte*, 22, 2603).

The following compound is a derivative of *dihydrobenzene*:—

Dihydrobenzaldehyde, $C_6H_7.CHO$. This results from a peculiar transposition of anhydro-ecgonine (*Berichte*, 23, 2880). It is an oil with a suffocating odor. It boils at 122° under a pressure of 120 mm. It exhibits all the properties of the fatty aldehydes, and reduces permanganate, and Fehling's solution at 100°. The oxide of silver oxidizes it to dihydrobenzoic acid.

AMIDE DERIVATIVES OF BENZALDEHYDE.

The action of ammonia upon benzaldehyde or benzyldichloride, $C_6H_5.CHCl_2$ (p. 715), produces **Tribenzylene-diamine**, $C_{21}H_{18}N_2 = (C_6H_5.CH)_3N_2$, or **Hydrobenzamide**, which crystallizes from alcohol and ether in rhombic octahedra, melting at 110°. It reacts neutral, and does not combine with acids; but as a tertiary diamine it forms with ethyl iodide a *Diammonium Iodide*, $C_{21}H_{18}N_2(C_2H_5I)_2$, which gives rise to the *ammonium oxide*, $C_{21}H_{18}N_2(C_2H_5)_2O$, with silver oxide; this yields crystalline salts with two equivalents of the acids.

When hydrobenzamide is boiled with alcohol or acids oil of bitter almonds and ammonia result.

Benzal-anilines are produced by heating hydrobenzamide with the anilines:—

$$(C_8H_5.CH)_3N_2 + 3H_2N.C_6H_5 = 3C_6H_5.CH{:}N.C_6H_5 + 2NH_3.$$

In a similar manner hydroxylamine forms benzaldoxime (*Berichte*, 22, 2887). If heated, hydrobenzamide is transposed to amarine (-Triphenyl-dihydroglyoxaline) (see Lophine).

The benzaldehydes combine with amines and anilines, forming benzylidene-, or benzal-amines and -anilines (p. 715). Acids resolve them into their components.

Benzylidene Ethylamine, $C_6H_5.CH:N.C_2H_5$, is an oil, boiling at 195°. **Benzylidene Aniline,** $C_6H_5.CH:N.C_6H_6$, **Benzal Aniline,** crystallizes in yellow needles, melting at 42°.

When benzaldehydes unite with the acid amides, *e.g.*, $C_2H_3O.NH_2$, the amid-hydrogen is not only entirely eliminated (p. 715), but two molecules of the amides are combined.

The *aldehydine bases*, resulting from the combination of benzaldehyde, with *o*-phenylene diamines, have already received mention (p. 628).

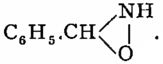
The benzaldehydes, like all aldehydes, unite with phenylhydrazine, forming phenylhydrazones (p. 656).

Benzylidene-Phenyl-Hydrazone, $C_6H_5.CH:N.NH.C_6H_5$, melts at 152.5°.

Benzaldoximes.

Benzaldoxime, $C_6H_7.CH(NOH)$, is formed by the action of hydroxylamine upon benzaldehyde. It is a thick oil. Sulphuric or hydrochloric acid will transform it into a crystalline *isomeride*, melting at 120–128° (*Berichte*, 23, 1684; 22, 432). These two compounds are readily converted into each other; they are soluble in alkalies. The sodium salt of the liquid α-aldoxime dissolves with difficulty in alcohol, while that of the β-variety is very soluble. Beckmann considers that these isomerides differ in structure as represented in the following formulas:—

(α) $C_6H_5.CH:N.OH$ and (β)

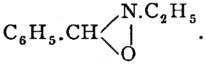


$$C_6H_5.CH\left\langle\begin{array}{l}NH\\ \,|\\ O\end{array}\right.$$

α-Benzaldoxime. β-Benzaldoxime.

When the sodium salts are alkylized, the α-variety yields an oxygen-ether, and the β-variety a nitrogen-ether:—

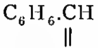
(α) $C_6H_5.CH:N.O.C_2H_5$ and (β)



$$C_6H_5.CH\left\langle\begin{array}{l}N.C_2H_5\\ \,|\\ O\end{array}\right.$$

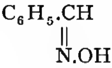
The two ethyl ethers and α-benzyl ether are oily liquids; β-**benzyl ether** melts at 82°. Hydrochloric acid decomposes the α-ethers into α-alkylhydroxylamines and the β-ethers into β-alkylhydroxylamines (p. 711). Conversely, the two benzylhydroxylamines convert benzaldehyde into the corresponding benzaldoxime-benzyl-ethers. In accordance with this we find that when the α-benzyl ether is heated with hydriodic acid the product is benzyl iodide, while the β-ether, under similar treatment, yields benzylamine (*Berichte*, 22, 1534). Ferricyanide of potassium oxidizes α- and β-aldoximes to azo-benzenyl peroxide, $C_{14}H_{12}N_2O_2$, and dibenzenyl azoxime, $C_{14}H_{10}NO$, which also result from benzil dioximes (*Berichte*, 22, 1590).

But two different **Cabanilido-benzaldoximes,** $C_6H_5.CH:N.O.CO.NH.C_6H_5$, have been obtained by the action of phenylisocyanate upon the two benzaldoximes (*Berichte*, 22, 3113). It is, therefore, concluded that the oxime groups have similar structure : N.OH, and that the two benzaldoximes are *stereochemical* isomerides (Goldschmidt, *Berichte*, 22, 3101; Hantzsch, *Berichte*, 23, 15, 20; Behrend, 23, 454). This view is confirmed by the behavior of the two anisaldoximes, $C_6H_4(O.CH_3).CH(N.OH)$, which yield, by alkylization, two different oxygen ethers, and indeed β-anisaldoxime forms a nitrogen ether at the same time. Hence, there are probably three *isomeric aldoximes*, two stereochemical isomerides, α and β, and a third, structurally isomeric form, called *isoaldoxime* (Goldschmidt, *Berichte*, 23, 2178; Behrend, *Berichte*, 23, 2750):—



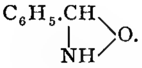
$$\begin{array}{r}C_6H_6.CH\\ \Vert\\ HO.N\end{array}$$

α-Aldoxime.



$$\begin{array}{l}C_6H_5.CH\\ \quad\Vert\\ \quad N.OH\end{array}$$

β-Aldoxime.



$$\begin{array}{l}C_6H_5.CH\\ \qquad\;|\\ \qquad NH\end{array}\!\!\Big\rangle O.$$

Isoaldoxime.

The aromatic, unsymmetrical ketones, containing two different radicals, *e.g.*, $\begin{matrix}C_6H_5\\C_7H_7\end{matrix}{>}CO$, also yield two ketoximes each (acetophenone- and pyroracemic-acid form but one). From this the isomerism of the oximes is dependent upon the asymmetry of the molecule in its relation to the nitrogen atom (Hantzsch, *Berichte*, 23, 2322, 2750). V. Meyer, abandoning his early views as to the cause of the isomerism of the oximes, believes now that the same is due to the spatial configuration of hydroxylamine (*Berichte*, 23, 2407).

SUBSTITUTION PRODUCTS OF BENZALDEHYDE.

The haloid benzaldehydes are obtained by substituting the nucleus of the benzyl chlorides, $C_6H_5.CH_2Cl$ and $C_6H_5.CHCl_2$. They can be prepared with less difficulty by oxidizing the haloid cinnamic acids with potassium permanganate (*Berichte*, 21, Ref. 253). Benzoyl chloride, $C_6H_5.CO.Cl$ (p. 580), is produced when chlorine is conducted into benzaldehyde.

NITROBENZALDEHYDES.

On dissolving benzaldehyde in nitric-sulphuric acid, or in a mixture of sulphuric acid with nitre (calculated amount) below 30–35°, the chief product is meta-nitrobenzaldehyde, which separates in a crystalline form. The oil (20–25 per cent.) consists principally of ortho-nitrobenzaldehyde, which cannot, however, be well obtained in pure form (*Berichte*, 14, 2802). *o*-Nitrobenzaldehyde is obtained pure from *o*-nitrobenzaldoxime (see below), when it is oxidized with a chromic acid mixture (*Berichte*, 14, 2334); also from *o*-nitrocinnamic ester through the action of nitric acid and sodium nitrite (*Berichte*, 14, 2803). *It is best obtained from o-nitro cinnamic acid*, by oxidizing the alkaline solution with potassium permanganate in the presence of benzene (*Berichte*, 17, 121).

Ortho-nitro-benzaldehyde, $C_6H_4(NO_2).CHO$, dissolves readily in alcohol and ether, but slightly in water, from which it crystallizes in long, yellowish needles. It melts at 46°, and distils with scarcely any decomposition. It possesses a peculiar odor, which is penetrating in the heat, and it distils with aqueous vapor. Potassium permanganate, or chromic acid, oxidizes it to *o*-nitrobenzoic acid; with concentrated sodium hydroxide *o*-nitrobenzyl alcohol and *o*-nitrobenzoic acid are readily produced. Potassium cyanide converts it into *o*-azoxybenzoic acid.

o-Nitro-benzaldehyde condenses with acetone, under the influence of a very little sodium hydroxide or baryta water (p. 730), to *o*-nitro-phenyl-lactic-methyl-ketone, $C_6H_4(NO_2).CH(OH).CH_2.CO.CH_3$, which with more caustic soda immediately splits off acetic acid and *indigo* (*Berichte*, **16**, 2205):—

$$2C_{10}H_{11}NO_4 + 2H_2O = C_{16}H_{10}N_2O_2 + 2C_2H_4O_2 + 4H_2O.$$

It condenses in the same manner with acetaldehyde to *o*-nitro-phenyl-lactic aldehyde, $C_6H_4(NO_2).CH(OH).CH_2.CHO$, and *o*-nitrophenyl-cinnamic aldehyde, $C_6H_4(NO_2).CH:CH.CHO$. The first of these also forms indigo with the alkalies.

With hydroxylamine, ortho-nitro-benzaldehyde yields the *aldoxime*, $C_6H_4(NO_2).CH(N.OH)$, melting at 95°. It results also from *o*-nitro-para-amidophenyl acetic acid by the action of nitrous acid, and then boiling with alcohol. It has been called nitroso-methyl-*o*-nitrobenzene (*Berichte*, **15**, 3057). Heated with hydrochloric acid, it is split up into NH_3 and *o*-nitrobenzoic acid; when oxidized (ferric chloride) it forms *o*-nitrobenzaldehyde with evolution of hyponitrous oxide.

The phenylhydrazine derivative, $C_6H_4(NO_2).CH(N_2H.C_6H_5)$, crystallizes in red needles, melting at 153° (*Annalen*, 232, 232).

Meta-nitro-benzaldehyde, $C_6H_4(NO_2).CHO$ (1, 3), results from the nitration of benzaldehyde (see above). It crystallizes from water in white needles, melting at 58°. When reduced it yields meta-amidobenzaldehyde, and when oxidized meta-nitrobenzoic acid. PCl_5 and reduction convert it into metatoluidine. It forms two aldoximes with hydroxylamine, one melting at 63°, and the other at 118° (*Berichte*, **23**, 2170). The latter is identical with the so-called nitroso-methyl-*m*-nitro-benzene (*Berichte*, **15**, 838 and 3060), obtained from *m*-nitro-*p*-amidophenyl acetic acid. Ferric chloride decomposes it into N_2O and *m*-nitrobenzaldehyde (*Berichte*, **15**, 2004).

PCl_5 converts the aldoxime into *m*-nitro-benzonitrile, $C_6H_4(NO_2).CN$. The *phenylhydrazone*, $C_6H_4(NO_2).CH:N_2H.C_6H_5$, consists of red needles, melting at 121°.

Para-nitro-benzaldehyde, $C_6H_4(NO_2).CHO$ (1, 4), results when *p*-nitrobenzyl chloride, $C_6H_4(NO_2).CH_2Cl$, is boiled with water, and lead nitrate, or when sulphuric acid acts upon *p*-nitrobenzal chloride, $C_6H_4(NO_2).CHCl_2$ (*Berichte*, **16**, 2539); finally, by the oxidation of *p*-nitrocinnamic acid with sulphuric acid and nitre (*Berichte*, **16**, 2714). It is most easily prepared by allowing CrO_2Cl_2 and water to act upon *p*-nitro-toluene (*Berichte*, **19**, 1061). It crystallizes from water in thin prisms, and melts at 107°. Its *aldoxime*, $C_6H_4(NO_2).CH(N.OH)$, melts at 128°, and decomposes into $NH_2.OH$ and *p* nitrobenzaldehyde (*Berichte*, **16**, 2003), when digested with acids. Its *phenylhydrazone*, $C_6H_4(NO_2).CH(N_2H.C_6H_5)$, melts at 155°.

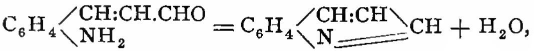
AMIDOBENZALDEHYDES.

These are obtained by the reduction of the nitrobenzaldehydes.

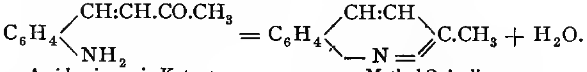
Ortho-amido-benzaldehyde, $C_6H_4(NH_2).CHO$ (1, 2), is best obtained by reducing ortho-nitrobenzaldehyde with ferrous sulphate and ammonia (*Berichte*, **17**, 456). It dissolves with difficulty in water, from which it crystallizes in silvery leaflets, melting at 40° to a yellowish oil. It possesses an intense odor, and volatilizes very readily in steam. It reduces an ammoniacal silver solution. Nitrous acid converts it into salicylic aldehyde.

Its *aldoxime*, $C_6H_4(NH_2).CH(N.OH)$, results by the reduction of *o*-nitrobenzaldoxime with ammonium sulphide. It melts at 133°, and when oxidized with $FeCl_3$, splits up into N_2O and *o*-amido-benzaldehyde (*Berichte*, **15**, 2004).

Ortho-amido-benzaldehyde yields condensation products with aldehydes, ketones and acids of the fatty series (p. 710). By the withdrawal of water (and inner condensation) these new compounds pass into quinoline derivatives (*Berichte*, 16, 1833):—

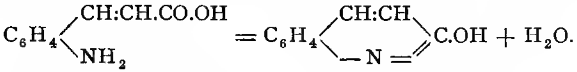


α-Amido-cinnamic Aldehyde. Quinoline.



o-Amido-cinnamic Ketone. α-Methyl Quinoline.

α-Oxyquinoline (carbostyril) is produced by condensation with acetic anhydride and sodium acetate:—



o-Amido-cinnamic Acid. α-Oxyquinoline.

With malonic acid it yields α-oxyquinoline carboxylic acid (*Berichte*, 17, 456).

Meta-amido-benzaldehyde, $C_6H_4(NH_2).CHO$ (1, 3), has not been obtained in a pure condition. It results in the reduction of *m*-nitrobenzaldehyde with stannous chloride or ferrous sulphate and ammonia; also by oxidizing its aldoxime with ferric chloride (*Berichte*, 15, 2044, and 16, 1997). By diazotizing it yields *m*-oxybenzaldehyde. Its *aldoxime*, $C_6H_4(NH_2).CH(N.OH)$, is obtained by the reduction of *m*-nitrobenzaldoxime with ferrous sulphate and ammonia. It melts at 88°.

Para-amido-benzaldehyde, $C_6H_4(NH_2).CHO$ (1, 4), is obtained from its aldoxime through the agency of acids. It crystallizes from water in leaflets, melting at 71°; these are not very stable. Its *aldoxime*, $C_6H_4(NH_2).CH(N.OH)$, is produced by the reduction of *p*-nitrobenzaldoxime. It melts at 124–129° (*Berichte*, 16, 2001).

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2. Toluic Aldehydes, $C_6H_4(CH_3).CHO$.

These can be easily obtained from the three xylenes, $C_6H_4(CH_3)_2$, through the action of CrO_2Cl_2 and water (p. 715) (*Berichte*, 17, 1464). The ortho- and meta-bodies resemble bitter-almond oil in odor.

o-Toluic Aldehyde results from ortho-xylyl chloride, $C_6H_4(CH_3).CH_2Cl$. It boils at 200°, and readily oxidizes, on exposure to the air, to *o*-toluic acid.

m-Toluic Aldehyde, obtained from meta-xylene chloride, boils at 199°, and when exposed, soon oxidizes to *m*-toluic acid. When nitrated, it yields an *o*-nitroaldehyde; this forms *methyl indigo* with acetone and caustic soda.

p-Toluic Aldehyde is obtained by the distillation of calcium paratoluate and formate. Its odor resembles that of peppermint; it boils at 204°, and is easily oxidized to *p*-toluic acid.

The so-called **α-Toluic Aldehyde**, $C_6H_5.CH_2.CHO$, **Phenylacetaldehyde**, is produced when chromyl chloride and water act upon ethyl benzene, $C_6H_5.C_2H_5$; by distillation of α-toluate of calcium and calcium formate; by heating β-phenyl-lactic acid or phenyl-oxy-acrylic acid with dilute sulphuric acid; from so-called phenyl-α-chlor-lactic acid, $C_6H_5.CH(OH).CHCl.CO_2H$, by the action of sodium hydroxide (*Berichte*, 16, 1286); or from phenyl-α-brom-lactic acid, $C_6H_5.CH(OH).CHBr.CO_2H$, with a soda solution (*Annalen*, 219, 179), and, finally, by acting with water on α-bromstyrolene. It is an oil, boiling at 206° and yielding benzoic acid upon oxidation with nitric acid. PCl_5 converts it into α-dichlorethyl benzene, $C_6H_5.CH_2.CHCl_2$ (p. 586). Nitration changes it into a compound which yields indol, C_8H_7N, when reduced or heated with zinc dust (*Be-*

richte, 17, 984). By the action of chloral and $AlCl_3$ upon benzene there is obtained the **Phenyldichloracetaldehyde**, $C_6H_5.CCl_2.CHO$, which reduces Fehling's and silver nitrate solutions, and oxidizes easily to the acid, $C_6H_5.CCl_2.CO_2H$ (*Berichte*, 17, Ref. 229).

3. **Phenyl-propyl Aldehyde**, $C_6H_5.CH_2.CH_2.CHO$, hydrocinnamic aldehyde, from hydrocinnamic acid, is an oil.

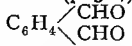
4. Aldehydes, $C_{10}H_{12}O$.

Cumic Aldehyde, $C_6H_4(C_3H_7).CHO$, **Cuminol**, is the isopropyl-benzaldehyde of the para-series. It occurs, together with cymene, $C_{10}H_{14}$, in Roman caraway oil, and in oil of *Cicuta virosa*, or water hemlock, etc. In order to effect its separation, shake the oil, boiling above 190°, with hydric sodic sulphite, press out the separated crystalline mass, and decompose it by distillation with sodium carbonate. Cuminol possesses an aromatic odor, has a specific gravity $= 0.973$ at 13°, and boils at 235°. Dilute nitric acid oxidizes it to cumic acid; chromic acid converts it into terephthalic acid. When distilled with zinc dust, the isopropyl group is transposed and ordinary cymene results.

It forms two aldoximes with hydroxylamine (*Berichte*, 23, 2175). Its hydrazone melts at 128°.

Nitro-Cuminol, $C_6H_3.(NO_2)(C_3H_7).CHO$, melts at 54°, and when acted upon by PCl_5, reduced, etc., yields thymol (p. 688).

Dialdehydes and Aldehyde-Alcohols (p. 324).



$C_6H_4\langle^{CHO}_{CHO}$

The *aldehydes of phthalic acid*, $C_6H_4\langle^{CHO}_{CHO}$ (ortho, meta and para), corresponding to the three acids, are produced (like the monovalent aldehydes) from the corresponding xylylene chlorides, $C_6H_4(CH_2Cl)_2$ and $C_6H_4(CHCl_2)_2$ (p. 573).

o-**Phthalaldehyde** is a thick oil, with an odor like that of oil of bitter almonds. Potassium permanganate oxidizes it quite readily to phthalic acid (*Berichte*, 20, 509). It combines with two molecules of hydroxylamine, yielding the di-aldoxime, $C_6H_4(CH:N.OH)_2$, melting at 245°.

m-**Phthalaldehyde** (isophthalaldehyde) crystallizes in long needles, melting at 89–90°. It is oxidized to isophthalic acid by $KMnO_4$ (*Berichte*, 20, 2005, 509). With hydroxylamine it forms a *di-aldoxime*, $C_6H_4(CH:N.OH)_2$, melting at 180°, and with acetyl chloride it yields *m*-dicyanbenzene, melting at 158°.

p-**Phthalaldehyde** (triphthalaldehyde), from *p*-xylylene-chloride by means of water and lead nitrate, consists of needles, soluble with difficulty in water and melting at 115°. When oxidized it yields terephthalic acid. Ammonia converts it into a di-imine and a hydrobenzamide derivative (*Berichte*, 19, 575). Potassium cyanide changes it to benzoïn-di-aldehyde (*Berichte*, 19, 1815). It yields a di-aldoxime with hydroxylamine, and a diacetyl ester with acetyl chloride.

Phenyl-lactic Aldehyde, $C_6H_5.CH(OH).CH_2\,CHO$, is an alcohol-aldehyde, produced by condensing benzaldehyde with acetaldehyde by means of very dilute soda-lye (p. 716). Acetic anhydride converts it into cinnamic aldehyde.

The three nitrobenzaldehydes similarly yield the corresponding **Nitrophenyl-lactic Aldehydes**, $C_6H_4(NO_2).CH(OH).CH_2\,CHO$. The *ortho*-body is very unstable, and when boiled with acetic acid anhydride yields *o*-nitrocinnamic aldehyde (p. 721). The *meta*-compound crystallizes from ether in needles, and decomposes about 100° (*Berichte*, 18, 720). The *para*-compound crystallizes with one molecule of aldehyde, which escapes at 115° (*Berichte*, 18, 372).

ALDEHYDE-PHENOLS OR OXY-ALDEHYDES.

The oxy-aldehydes, having hydroxyl in the benzene nucleus, are obtained by oxidizing (p. 713) the oxy-alcohols with chromic acid. An important synthetic method, wherein the aldehyde group is directly introduced, consists in letting chloroform and an alkaline hydroxide act upon phenols (reaction of Reimer):—

$$C_6H_5.OH + CHCl_3 + 4KOH = C_6H_4\begin{cases}OK \\ CHO\end{cases} + 3KCl + 3H_2O.$$

All the benzene oxy-derivatives (the oxyacids also) react similarly; hence, innumerable oxy-aldehydes have been prepared.

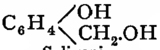
To perform the reaction, dissolve the phenol and some potassium or sodium hydroxide in 1½–2 parts water, and while heating on a water bath, in connection with a return condenser, gradually add chloroform. Chloral can be substituted for the latter. The excess of chloroform is distilled off, the residue supersaturated with hydrochloric or sulphuric acid, and the separated aldehyde finally extracted with ether. Ortho-formic phenyl ether is produced at the same time (p. 671).

It is very probable the reaction proceeds in such a manner that formic acid first results from the action of the alkali on chloroform: $CHCl_3 + 4KOH = CHO.OK + 3KCl + 2H_2O$ (p. 217) and as it is produced, acts on the phenol. Oxy-acids are obtained in the same way, when CCl_4 is employed. In this reaction, very frequently the CO_2H-group, occupying the para-position in the oxy-acids (para-oxy-benzoic acid), is exchanged for CHO (*Berichte*, 9, 1268).

In deportment the oxyaldehydes are perfectly analogous to the monovalent benzaldehydes. They reduce an ammoniacal silver solution, but not the Fehling solution. Oxidizing agents convert them with difficulty into oxyacids; this is most easily accomplished by fusion with caustic alkalies. They dissolve in alkalies, forming salts *e. g.*, $C_6H_4(CHO).ONa$; the alkyl iodides convert the latter into alkyl ethers (p. 668). They give aldoximes with hydroxylamine.

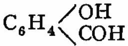
1. *Oxybenzaldehydes*, $C_6H_4(OH).CHO$.

Ortho-oxybenzaldehyde (1, 2), **Salicylic Aldehyde,** occurs in the volatile oils of the different varieties of *Spiræa*. It is obtained by the oxidation of saligenin and salicin (p. 713), but is most readily prepared (together with para-oxybenzaldehyde) by the action of chloroform and caustic potash upon phenol (*Berichte*, 10, 213). An oil, with an aromatic odor; solidifies at —20°, and boils at 196°; its specific gravity = 1.172 at 15°. It volatilizes readily with steam. It is rather easily soluble in water; the solution is colored a deep violet by ferric chloride. It colors the skin an intense yellow. Sodium amalgam transforms it into saligenin; oxidizing agents change it to salicylic acid:—



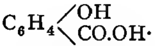
$C_6H_4\Big\langle\begin{matrix}OH\\CH_2.OH\end{matrix}$

Saligenin.



$C_6H_4\Big\langle\begin{matrix}OH\\COH\end{matrix}$

Salicylic Aldehyde.



$C_6H_4\Big\langle\begin{matrix}OH\\CO.OH\end{matrix}$

Salicylic Acid.

Salicylic aldehyde dissolves in caustic potash to form the crystalline derivative, $C_6H_4(OK)CHO$, from which ethers are obtained through the agency of alkyl iodides. The *methyl ether*, $C_6H_4(O.CH_3).CHO$, melts at 35°, and boils at 238°; the *ethyl ether* boils at 248°. *Salicyl aldoxime*, $C_6H_4(OH).CH(N.OH)$, melts at 57°.

Consult *Berichte*, **22**, 2339, upon the nitrosalicylaldehydes.

Meta-oxybenzaldehyde (1, 3) results together with the alcohol in the reduction of *m*-oxybenzoic acid with sodium amalgam, and from *m*-nitrobenzaldehyde by reduction and diazotizing (*Berichte*, **15**, 2044). It crystallizes from hot water in white needles, melts at 104°, and boils near to 240°. Its *hydrazone* melts at 131°. Its nitration produces three mononitro-compounds. A fourth *p*-nitro-*m*-oxybenzaldehyde has been obtained from *m*-nitrobenzaldehyde, and it cannot, contrary to statement (*Berichte*, 18, 2572) be converted into vanillin.

Para-oxybenzaldehyde is formed from phenol, together with salicylic aldehyde; also by the reduction of para-oxybenzoic acid, and by heating anisic aldehyde to 200° with hydrochloric acid. It is rather easily soluble in hot water, crystallizes in small needles, melts at 116°, and sublimes. Ferric chloride colors it the same as phenol. It yields para-oxybenzoic acid on fusion with KOH. Its *aldoxime* melts at 65°; its *hydrazone* at 178°. Its methyl ether is the so-called—

Anisic Aldehyde, $C_6H_4(O.CH_3).CHO$, which results in oxidizing various essential oils (anise, fennel, etc.) with dilute nitric acid, or a chromic acid mixture. A soda solution will liberate it from its crystalline compound with sodium bisulphite. It is a colorless oil of specific gravity 1.123 at 15°, and boils at 248°. It combines with hydroxylamine to yield two *aldoximes* (p. 718).

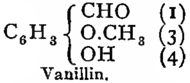
2. *Dioxybenzaldehydes*, $C_7H_6O_3 = C_6H_3(OH)_2.CHO$.

Three of the six possible isomerides have been prepared from the dioxybenzenes, $C_6H_4(OH)_2$, by means of the chloroform reaction; likewise, six methyl dioxybenzaldehydes, $C_6H_3.(O.CH_3).(OH).CHO$, have been obtained from the three mono-methyl-dioxybenzenes (*Berichte*, 14, 2024). Dialdehydes also are simultaneously produced in dilute solutions when CCl_3H and KOH are employed.

β-Resorcyl Aldehyde, $C_6H_3(OH)(OH).CHO$ (1, 3, 4), obtained from resorcinol, melts at 135°, and with acetic anhydride yields (according to Perkin) umbelliferon. **Gentisin Aldehyde**, $C_6H_3(OH)(OH).CHO$ (1, 4, CHO), from hydroquinone, melts at 99°, and yields gentisinic acid on oxidation.

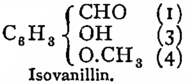
Protocatechuic Aldehyde, $C_6H_3(OH)(OH).CHO$ (1, 3, 4—CHO in 1), the parent substance of vanillin and piperonal, was first obtained from the latter; it is prepared synthetically from pyrocatechin by the chloroform reaction (*Berichte*, 14, 2015); also by heating its ethers, vanillin, isovanillin and piperonal, with dilute hydrochloric acid to 200°, and from opianic acid. It dissolves readily in water, forms brilliant crystals (from toluene), and melts at 150°. It reduces silver solutions with the production of a mirror, and combines with alkaline bisulphites. Ferric chloride colors its aqueous solution a deep *green* (p. 690).

Protocatechuic aldehyde is a derivative of homopyrocatechin (p. 693); its acid is protocatechuic acid (see this). Its important ethers are vanillin, isovanillin and piperonal:—



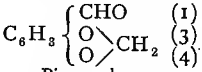
$$C_6H_3\begin{cases}CHO & (1)\\ O.CH_3 & (3)\\ OH & (4)\end{cases}$$

Vanillin.



$$C_6H_3\begin{cases}CHO & (1)\\ OH & (3)\\ O.CH_3 & (4)\end{cases}$$

Isovanillin.



$$C_6H_3\begin{cases}CHO & (1)\\ O\diagdown CH_2 & (3)\\ O\diagup & (4)\end{cases}$$

Piperonal.

The two OH groups in protocatechuic aldehyde occupy the ortho-position, but the CHO group the para with reference to one of the OH groups (see protocatechuic acid). For the position of the methyl group in vanillin see *Berichte*, 9, 1283, and 11, 125; it is intimately related to creosol (p. 693).

Vanillin, $C_8H_8O_3$, methyl protocatechuic aldehyde, is the active and odorous constituent of the vanilla bean pods (about two per cent.). It was first prepared artificially from the glucoside coniferine, by its oxidation with chromic acid (Tiemann), a procedure now applied technically for the obtainment of vanillin. It is formed synthetically, together with an isomeric aldehyde, when guaiacol is acted upon by chloroform and caustic alkali (*Berichte*, 14, 2021), and by oxidizing eugenol from clove-oil.

Glycovanillin, $C_6H_3(O.CH_3)(O.C_6H_{11}O_5).CHO$, the glucoside of vanillin, is produced when coniferine is oxidized by chromic acid. It crystallizes from dilute alcohol in white needles, melting at 192°. Acids or emulsin split it up into glucoses and vanillin (*Berichte*, 18, 1595, 1657).

Vanillin crystallizes in stellate groups of needles, is soluble in hot water, alcohol and ether, melts at 80–81°, and sublimes. As a phenol it forms salts with one equivalent of a base; as an aldehyde it combines with primary alkaline sulphites. Heated with HCl to 180° it decomposes into CH_3Cl and protocatechuic aldehyde. Protocatechuic acid results on fusion with potassium hydroxide (the aldehyde group is oxidized and methyl split off). Nascent hydrogen converts vanillin into vanillin alcohol (p. 714); energetic oxidation carries it to vanillinic acid.

Coniferine, $C_{16}H_{22}O_8 + 2H_2O$, is found in the cambium of coniferous woods, and consists of shining needles. It effloresces in the air, and melts at 185°. It acquires a dark blue color when moistened with phenol and hydrochloric acid. Boiling acids or emulsin decompose it into glucoses and *Coniferyl Alcohol*, $C_{10}H_{12}O_3 = C_6H_3\begin{pmatrix}O.CH_3\\ OH\end{pmatrix}.C_3H_4.OH$; the latter melts at 75°, and is oxidized to vanillin (together with homovanillin) by chromic acid.

Isovanillin (see above) is obtained by oxidizing hesperitinic acid or by heating opianic methyl ether with hydrochloric acid.

Dimethylprotocatechuic Aldehyde, $C_6H_3(O.CH_3)_2CHO$ Methylvanillin, is obtained from vanillin by the action of methyl iodide and potassium hydroxide. It is not very soluble in water, melts about 20°, and boils near 285°. It yields dimethylprotocatechuic acid by oxidation.

Piperonal, $C_8H_6O_3$, heliotropine, obtained by oxidizing piperic acid (see this) is the methylene ether of protocatechuic aldehyde (p. 724). It consists of crystals which dissolve with difficulty in water, melt at 37° and boil at 263°. Being an aldehyde it unites with primary alkaline sulphites. When oxidized it forms piperonylic acid, when reduced piperonyl alcohol (p. 714).

Bi-di-oxymethylene indigo is obtained from its nitro-derivative (*Berichte*, 23, 1566).

PCl_5 converts it into the chloride, $C_6H_3(O_2:CCl_2)CHCl_2$, which yields protocatechuic aldehyde when boiled with water; the group CCl_2 splits off.

KETONES.

The ketones in which two benzene nuclei are joined by the ketonic group CO, *e. g.*, benzophenone, $C_6H_5.CO.C_6H_5$, will receive attention later. At this point we will only consider the *mixed* ketones, containing a benzene and also an alkyl group:—

$$C_6H_5.CO.CH_3, \text{ Acetophenone.}$$

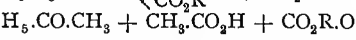
These are perfectly analogous to the ketones of the paraffin series, and are obtained by similar methods, chiefly by the distillation of a mixture of calcium salts of an aromatic and a fatty acid (p. 187). They also result when (1) sulphuric acid (diluted ½ volume) acts on the phenylacetylenes (pp. 87 and 204):—

$$C_6H_5.C{:}CH + H_2O = C_6H_5.CO.CH_3;$$

(2) or from the benzenes on boiling with fatty acid chlorides and $AlCl_3$, as well as from the phenol ethers, unsaturated homologous benzenes being formed together with the ketones (*Berichte*, 23, 1199):—

$$C_6H_6 + CH_3.COCl = C_6H_5.CO.CH_3 + HCl,$$
$$C_6H_5.O.CH_3 + CH_3.CO.Cl = C_6H_4(O.CH_3).CO.CH_3 + HCl;$$

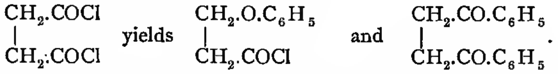
(3) and by the decomposition of benzoyl acetic esters (p. 341) when they are boiled with water or sulphuric acid (30 per cent.):—



$$C_6H_5.CO.CH\left\langle\begin{matrix}CO.CH_3\\CO_2R\end{matrix}\right. + 2H_2O =$$
$$C_6H_5.CO.CH_3 + CH_3.CO_2H + CO_2R.OH.$$

Benzoyl acetones (β-diketones) are produced at the same time as intermediate products (in slight amount), *e. g.*, $C_6H_6.CO.CH_2.CO.CH_3$. They dissolve in alkalies, and are precipitated by CO_2. The nitro-benzoyl aceto-acetic esters deport themselves similarly (*Berichte*, 16, 2239; *Annalen*, 221, 332). Thus from aceto-phenone-bromide, $C_6H_6.CO.CH_2Br$, we obtain bodies with aceto-acetic esters, from which, by decomposition, the *γ-diketones* of the type $C_6H_5.CO.CH_2.CH_2.CO.CH_3$, are obtained; these are insoluble in alkalies.

γ-Diketones like these are also formed by the action of succinyl chloride upon benzenes in the presence of $AlCl_3$; ketonic acid chlorides are produced simultaneously (*Berichte*, 20, 1374; 21, Ref. 611):—



$$\begin{matrix} CH_2.COCl \\ | \\ CH_2.COCl \end{matrix} \text{ yields } \begin{matrix} CH_2.O.C_6H_5 \\ | \\ CH_2.COCl \end{matrix} \text{ and } \begin{matrix} CH_2.CO.C_6H_5 \\ | \\ CH_2.CO.C_6H_5 \end{matrix}.$$

The benzene ketones are oils, insoluble in water, and boil without decomposition; phenyl methyl ketone is the only one that is a solid. With the exception of benzyl-methyl ketone they do not unite with alkaline bisulphites. Nascent hydrogen converts them into secondary alcohols which form ketones when oxidized.

Chromic acid transforms the ketones $C_6H_5.COR$ into benzoic acid and the alkyl, which is further oxidized (p. 203).

Cold potassium permanganate converts a few of them into α-ketonic acids (*Berichte*, 23, Ref. 640). Acids and acid amides (*Berichte*, 21, 534) are formed when phenylmethyl ketones are heated with yellow ammonium sulphide:—

$$C_6H_5.CO.CH_3 \text{ yields } C_6H_6.CH_2.CO_2H \text{ and } C_6H_5.CH_2.CO.NH_2.$$

On heating benzene ketones with concentrated or fuming sulphuric acid the acetyl-group splits off and benzenesulphonic acids result (*Berichte*, 19, 2623).

The phenyl-alkyl ketones apparently form but *one* acetoxime with hydroxylamine (p. 205); whereas, the unsymmetrical ketones, having two phenyl groups, yield two acetoximes. All ketones form *hydrazones* with phenylhydrazine.

---

(1) **Phenyl-methyl-ketone**, $C_6H_5.CO.CH_3$, Acetophenone, results by the action of zinc methyl upon benzoyl chloride, $C_6H_5.COCl$, and is obtained by distilling benzoate of calcium (100 parts) with calcium acetate (56 parts). The most convenient method consists in boiling benzene (10 parts) with acetyl chloride (1 part) and $AlCl_3$ (2 parts).

It crystallizes in large plates, melts at 20.5°, and boils at 202°.

It is applied as a hypnotic under the name of *hypnone*. Nascent hydrogen converts it into phenyl-methyl carbinol (p. 711). Chromic acid and potassium permanganate oxidize it to benzoic acid, while a slight amount of phenyl-glyoxylic acid (*Berichte*, 23, 648) is produced by ferricyanide of potassium or permanganate.

Its *acetoxime*, $C_6H_5.C(N.OH).CH_3$, melts at 59°, and by the action of concentrated sulphuric acid, or of HCl in glacial acetic acid is converted into isomeric acetanilide:—

$$C_6H_5.C(N.OH).CH_3 \text{ yields } C_6H_5.NH.CO.CH_3.$$

Other ketoximes behave in an analogous manner (transposition of Beckmann) (*Berichte*, 20, 1509, 2581; 23, 2746).

The phenyl-hydrazone, $C_6H_5.CH_3.C:N.NH.C_6H_5$, melts at 105°. Acetophenone affords β-dichlorethyl benzene with PCl_5.

The chlorination of boiling acetophenone produces the so-called **Acetophenone Chloride**, $C_6H_5.CO.CH_2Cl$, melting at 59°, and boiling at 245°. The *bromide*, $C_6H_5.CO.CH_2Br$, results in the action of bromine on acetophenone dissolved in CS_2 (on passing CO_2 through the solution) (*Berichte*, 16, 22). It crystallizes in large, rhombic prisms, melting at 50°; its vapors provoke tears. The further bromination of acetophenone in carbon disulphide solution produces **Acetophenone-dibromide**, $C_6H_5.CO.CHBr_2$, melting at 37°; alcoholic ammonia converts it into benzamide, $C_6H_5.CO.NH_2$, and KOH changes it to mandelic acid, $C_6H_5.CH(OH).CO_2H$. With hydroxylamine, acetophenone dibromide, $C_6H_5.CO.CHBr_2$, and monobromide yield *Phenylglyoxime*, $C_6H_5.C(N.OH).CH(N.OH)$ (p. 207), melting at 162° (*Berichte*, 22, 419). Phenylhydrazine and bromacetophenone yield the base $(C_{14}H_{12}N_2)_2$ (*Berichte*, 23, Ref. 501).

Ammonia converts the chloride or bromide into *isoindol*, $C_{16}H_{14}N_2$, identical with diphenylpyrazine (*Berichte*, 21, 19, 1278).

The acid amides convert acetophenone into peculiar oxygen *bases*, in which, in all probability, the oxazole ring is present (*Berichte*, 21, 924).

Aniline and bromacetophenone yield an anilide, which condenses to α-phenylindol (*Berichte*, 21, 1071).

In the same manner, methyl- and dimethyl-aniline produce acetophenone-methyl-anilide, $C_6H_5.CO.CH_2.N(CH_3).C_6H_5$; this also condenses, yielding *n*-methyl-α-phenyl indol (*Berichte*, 21, 2196, 2595) (see indol).

In the action of sodium ethylate upon a mixture of acetophenone and amyl nitrite, a peculiar reaction (Claisen) occurs, according to the equation—

$$C_6H_5.CO.CH_3 + NO.O.C_2H_5 = C_6H_5.CO.CH(N.OH) + C_2H_5OH,$$

whereby we obtain:—

Isonitroso-acetophenone, $C_6H_6.CO.CH(N.OH)$. This crystallizes from alcohol in shining prisms, melting at 127° and decomposing at 155° (*Berichte*, 20, 2194). It forms isoindol by reduction.

Nitro-acetophenones, $C_6H_4(NO_2).CO.CH_3$.

The meta-body is the chief product (just as in the case of benzaldehyde) when acetophenone is dissolved in cold, fuming nitric acid. An isomeric oil is formed at the same time. The three isomerides can be prepared from the three nitrobenzoyl-aceto-acetic esters, which result from the action of the nitrobenzoyl chlorides, $C_6H_4(NO_2).COCl$, upon aceto-acetic esters (p. 726).

o-**Nitro-acetophenone** is a yellowish oil, of peculiar odor, and does not solidify on cooling. Bromine converts it into a mono- and a di-bromide, from which indigo is obtained by the action of ammonium sulphide (*Annalen*, 221, 330).

m-**Nitro-acetophenone** crystallizes in needles, melts at 93°, volatilizes with steam, and is oxidized to *m*-nitrobenzoic acid by potassium permanganate.

p-**Nitro-acetophenone** results on digesting *p*-nitrophenyl-propiolic acid, $C_6H_4(NO_2)C:C.CO_2H$, with sulphuric acid; it first parts with CO_2 and the resulting nitrophenyl-acetylene, $C_6H_4(NO_2).C:CH$, absorbs water (p. 726). *p*-Nitro-acetophone forms yellowish prisms, melts at 80°, and with PCl_5 yields *p*-nitro-chlor-styrol, $C_6H_4(NO_2).CCl:CH_2$ (*Annalen*, 212, 159).

Amido-acetophenones, $C_6H_4(NH_2).CO.CH_3$.

o-**Amido-acetophenone** (1, 2) is obtained: By reducing *o*-nitroacetophenone with tin and hydrochloric acid; from *o*-amido-phenyl acetylene, $C_6H_4(NH_2)C:CH$, by the action of sulphuric acid; by boiling *o*-amidophenyl-propiolic acid with water

(*Berichte*, 15, 2153); and in slight quantity on heating acetanilide, $C_6H_5.NH.CO.CH_3$, with $ZnCl_2$ (p. 607). It is a thick, yellow oil, which boils at 242°–252°, and possesses a characteristic sweetish, lasting odor. A pine splinter, dipped into the aqueous solution of its hydrochloride, is colored an intense orange-red. It is very stable, and cannot form an inner condensation product. Acetic anhydride converts it into the acetate, $C_6H_4(NH.C_2H_3O).CO.CH_3$; the bromides of the latter yield *indigo* when shaken with sodium hydroxide and air (*Berichte*, 17, 963).

m-**Amido-acetophenone** results on reducing *m*-nitro-acetophenone. It consists of yellow crystals, melting at 93°. *p*-**Amido-acetophenone** is obtained by reducing the *p*-nitro body, and also on boiling aniline with acetic anhydride and $ZnCl_2$ (*Berichte*, 18, 2688). It crystallizes in flat needles, and melts at 106°.

Oxyacetophenones, or Ketophenols.

These are produced when di- and tri-hydric phenols are heated with glacial acetic acid and $ZnCl_2$ to 160° (*Berichte*, 23, Ref. 43).

α-Naphthol reacts in a similar manner (*Berichte*, 21, 322). Ethers of ketophenols are produced by the action of phenol ether upon acid chlorides in the presence of $AlCl_3$ (p. 726). Alkyl benzenes are simultaneously produced (*Berichte*, 23, 1199). Propionyl chloride converts phenol into phenol propionic esters and *propionyl phenol*, $C_6H_4(CO.C_2H_5).OH$ (*Berichte*, 22, Ref. 746).

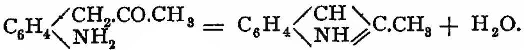
Resacetophenone, $C_6H_3(OH)_2.CO.CH_3$, from resorcinol, melts at 142°, and may be obtained by fusing β-methyl umbelliferon with potassium hydroxide. **Quinacetophenone**, $C_6H_3(OH)_2.CO.CH_3$, from hydroquinone, melts at 202°. **Gallacetophenone**, $C_6H_2(OH)_3.CO.CH_3$, from pyrogallic acid, melts at 168°.

(2) **Phenyl-ethyl Ketone**, $C_6H_5.CO.C_2H_5$, *propiophenone*, results when a mixture of calcium benzoate and propionate is distilled, or when zinc ethyl acts upon benzoyl chloride, $C_6H_5.COCl$, and by the action of $AlCl_3$ upon benzene and propionyl chloride. It boils at 208–210°. Nascent hydrogen converts it into secondary phenyl-propyl alcohol (p. 711); chromic acid breaks it up into benzoic and acetic acids. Amyl nitrite converts it into phenyl-isonitroso-ethyl ketone, $C_6H_5.CO.C(N.OH).CH_3$, melting at 109° (*Berichte*, 22, 529).

Phenyl-propyl Ketone, $C_6H_6.CO.C_3H_7$, obtained from calcium benzoate and butyrate, boils at 220–222°. Chromic acid decomposes it into benzoic and propionic acids. The isomeric **Phenylisopropyl Ketone**, $C_6H_5.CO.C_3H_7$, from calcium benzoate and isobutyrate, boils at 215°, and is converted into henzoic, acetic and carbonic acids by chromic acid.

Phenylketones of the higher alkyls, like $C_6H_5.CO.C_4H_9$ and $C_6H_5.CO.C_5H_{11}$, have been prepared from mono- and di-alkylic benzoyl acetic esters, $C_6H_5.CO.CHR.CO_2R$ and $C_6H_5.CO.CR_2.CO_2R$ (p. 726) by a ketone decomposition induced by alcoholic potash.

3. **Benzyl-methyl Ketone**, $C_6H_5.CH_2.CO.CH_3$, *Phenyl acetone*, results in the distillation of calcium alphatoluate and acetate, and when zinc methyl acts on alphatoluic chloride, $C_6H_6.CH_2.COCl$. It boils at 214–216°, unites with primary sodium sulphite, and decomposes with chromic acid into benzoic and acetic acids. When its *nitro*-product is treated with zinc dust and ammonia an amido-derivative of the ortho series is first formed—$C_6H_4(NH_2).CH_2.CO.CH_3$, but this loses water and becomes methyl ketol:—

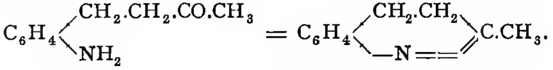


$$C_6H_4\left\langle\begin{matrix}CH_2.CO.CH_3\\NH_2\end{matrix}\right. = C_6H_4\left\langle\begin{matrix}CH\\NH\end{matrix}\right\rangle C.CH_3 + H_2O.$$

Methyl Ketol.

Benzyl-ethyl Ketone, $C_6H_5.CH_2.CO.C_2H_5$, results from α-toluic chloride by the action of zinc ethyl. It boils at 226°, and is oxidized by chromic acid to benzoic and propionic acids.

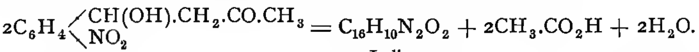
Phenyl-ethyl-methyl Ketone, $C_6H_5.CH_2.CH_2.CO.CH_3$, *Benzyl acetone*, is formed from calcium hydro-cinnamate and acetate, and from benzyl aceto-acetic ester (p. 340). It boils at 235°, and when the nitro product is reduced condensation ensues in the ortho-amido-derivative first produced, with formation of hydromethyl quinoline, $C_{10}H_{13}N$:—



Hydromethyl Quinoline.

An oxy-derivative of phenyl-ethyl-methyl ketone is *Phenyl-lactic acid—Methyl Ketone*, $C_6H_5.CH(OH).CH_2.CO.CH_3$. The ortho- and para-nitro-derivatives of the latter are obtained by the condensation of ortho- and paranitrobenzaldehyde by means of very dilute sodium hydroxide (p. 723).

o-**Nitrophenyl-lactic acid-Methyl Ketone** forms large crystals, melting at 69°. When acted upon by excess of sodium hydroxide, or when boiled with water, it at once (by the union of two molecules and the elimination of two molecules of acetic acid) yields indigo (Baeyer, *Berichte*, 15, 2857) :—



$$2C_6H_4\left\langle\begin{array}{l}CH(OH).CH_2.CO.CH_3\\NO_2\end{array}\right. = C_{16}H_{10}N_2O_2 + 2CH_3.CO_2H + 2H_2O.$$

Indigo.

When heated with acetic anhydride it splits off water and becomes *o*-nitrobenzylidene acetone, $C_6H_4(NO_2).CH{:}CH.CO.CH_3$.

p-Nitrophenyl-lactic acid-Methyl Ketone, from *p*-nitrobenzaldehyde, melts at 58°, and when boiled with acetic anhydride yields *p*-nitrobenzylidene acetone (*Berichte*, 16, 1968).

4. Methyl ketones of the homologous benzenes are readily obtained by the action of acetyl chloride or acetic anhydride upon benzenes in the presence of $AlCl_3$ (p. 726).

p-Tolyl-methyl-ketone, $C_6H_4(CH_3).CO.CH_3$, acetyl toluene, is obtained from cymene by the action of concentrated nitric acid (p. 577). It is a colorless liquid, boiling at 224°. Nitric acid oxidizes it to paratoluic acid and chromic acid to terephthalic acid. See *Berichte*, 21, 2265, for higher tolylalkyl ketones.

Xylylmethyl Ketones, $C_6H_3(CH_3)_2.CO.CH_3$: The *ortho* (from orthoxylene) boils at 243°, the *meta* at 228°, and the *para* at 224°.

See p. 518 for phenyl trimethylene ketone,  $C_6H_5.CO.CH\left\langle\begin{array}{l}CH_2\\CH_2\end{array}\right\rangle$, or benzoyl trimethylene.

Keton-aldehydes or Aldehyde Ketones (p. 323).

Benzoyl Formic Aldehyde, $C_6H_5.CO.CHO$, phenyl glyoxal, is obtained from isonitroso-acetophenone, $C_6H_5.CO.CH(NOH)$ p. 728). It crystallizes from water as a hydrate, melting at 73°. It volatilizes in a current of steam and provokes sneezing (*Berichte*, 22, 2557). Phenylhydrazine converts it into a hydrazone and an osazone. Alkalies convert it into mandelic acid, $C_6H_5.CH(OH).CO_2H$.

Toluyl Formic Aldehyde, $C_6H_4(CH_3).CO.CHO$, from isonitrosotolylmethyl ketone, also crystallizes as a hydrate, melting about 100°.

Benzoylaldehyde, $C_6H_5.CO.CH_2.CHO$, is a β-ketone aldehyde. It is obtained by the condensation of acetophenone and formic ester by means of sodium ethylate (Claisen, p. 323): $C_6H_5.CO.CH_3 + CHO.O.C_2H_5 = C_6H_5.CO.CH_2.CHO + C_2H_5.OH$. The sodium compound first forms, and from this acetic acid liberates the aldehyde ketone, as a yellow, very unstable oil. It resembles the β ketonaldehydes of the fatty series very much, and is colored an intense red by ferric chloride. It condenses with phenyl-hydrazine to diphenyl-pyrazole (*Berichte*, 21, 1135).

Diketones (see p. 325).

α- or Orthodiketones, $C_6H_5.CO.CO.R$, are produced by replacing the isonitroso-group of the isonitroso ketones (p. 325).

Benzoyl Acetyl, $C_6H_5.CO.CO.CH_3$, from isonitroso-ethyl-phenyl ketone, $C_6H_5.CO.C(N.OH).CH_3$ (p. 730), is a yellow oil with a peculiar odor (*Berichte*, 21, 2176; 22, 527).

The β- or meta-diketones, $C_6H_5.CO.CH_2.CO.R$, result from the decomposition of the benzoyl-acetoacetic esters (p. 726); further by a remarkable condensation, induced by sodium alcoholate (Claisen, *Berichte*, 20, 2178). Thus, benzoyl acetone is obtained from benzoic ester and acetone, and from acetophenone and acetic ester:—

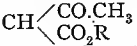
$$C_6H_5.CO.O.C_2H_5 + CH_3.CO.CH_3 = C_6H_5CO.CH_2.CO.CH_3 + C_2H_5.OH.$$
$$C_6H_5.CO.CH_3 + CH_3.CO.OR = C_6H_5CO.CH_2.CO.CH_3 + C_2H_5.OH.$$

Ketonic acids are similarly produced (see these); while the formation of benzoyl aldehyde from acetophenone and formic ester (see below), and that of isonitroso-phenone are analogous (p. 728).

The β-diketones behave like the β-diketones of the fatty series. They dissolve in alkalies. This distinguishes them from the other diketones. They are colored an intense red by ferric chloride. They form pyrazole compounds with phenyl hydrazine.

Benzoyl Acetone, $C_6H_5.CO.CH_2.CO.CH_3$ (see above), acetyl acetophenone, is most readily prepared by the action of acetic ester and sodium ethylate upon acetophenone (*Berichte*, 20, 2180). It melts at 60–61°, boils at 260–262°, and readily volatilizes with steam. It forms an oxime-anhydride, $C_{10}H_9NO$ (*Berichte*, 21, 1150) with hydroxylamine. Alkyl derivatives have not been prepared. *o*-**Nitrobenzoyl Acetone**, $C_6H_4(NO_2).CO.CH_2.CO.CH_3$, from *o*-nitrobenzoyl acetic ester, melts at 55°.

Propionyl acetophenone, $C_6H_5.CO.CH_2.CO.C_2H_5$, etc., have been prepared in an analogous manner by the condensation of acetophenone with higher fatty acid esters (*Berichte*, 20, 2181).

Phenyl-acetyl-acetone, $C_{11}H_{12}O_2 = C_6H_5.CH_2.CO.CH_2.CO.CH_3$, results from the decomposition of phenyl acetyl-acetoacetic ester, $C_6H_5.CH_2CO.$  $CH\left\langle\begin{matrix}CO.CH_3\\CO_2R\end{matrix}\right.$ (from $C_6H_5.CH_2.COCl$ and acetoacetic ester). It is an oil boiling about 268°. It yields a pyrazole derivative with phenylhydrazine (*Berichte*, 18, 2137).

The following is a γ-diketone (p. 328):—

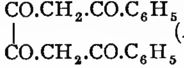
Acetophenone-acetone, $C_6H_5.CO.CH_2.CH_2.CO.CH_3$, is obtained from acetophenone aceto-acetic ester (p. 727). It is a yellow oil, insoluble in alkalies, and not volatile with aqueous vapor (*Berichte*, 17, 2756).

Being a γ-diketone it can split off water and yield phenylmethylfurfurane. P_2S_5 converts it into phenylmethylthiophene, while ammonia changes it to phenylmethyl pyrrol (p. 329).

The analogous ketones: diphenacyl, dibenzoyl methane, and tribenzoyl methane, will be discussed under the compounds containing several benzene nuclei.

Mixed Triketones: *Dibenzoyl Acetone*, $(C_6H_5.CO)_2CH.CO.CH_3$, from sodium benzoyl acetone and benzoyl chloride, melts at 102°. The hydrogen of its CH-group cannot be replaced by sodium or alkyls (*Berichte*, 21, 1153). *Triacetyl Benzene*, $C_6H_3(CO.CH_3)_3(1, 3, 5)$, results from the condensation of acetaldehyde. It melts at 163°. It may be oxidized to trimesic acid (*Berichte*, 21, 1145).

Oxalyl-diacetophenone,



$$\begin{array}{l}CO.CH_2.CO.C_6H_5\\ |\\ CO.CH_2.CO.C_6H_5\end{array}$$

(*Berichte*, 21, 1134), is a tetraketone.

NITRILES.

The nitriles of the benzene series, the compounds of the benzene nucleus with the cyanogen group, are formed, like the fatty nitriles, by distilling the alkali benzene sulphonates with potassium cyanide or yellow prussiate of potash (p. 659), and by the action of P_2O_5 or PCl_5 upon the ammonium salts and amides of the aromatic acids (p. 282).

When the halogene benzene sulphonic acids are distilled with CNK the halogen atoms are also replaced by cyanogen groups and we get dicyanides:—

$$C_6H_4Br.SO_3K + 2CNK = C_6H_4(CN)_2 + SO_3K_2 + BrK.$$

The direct replacement of the halogens in the benzene hydrocarbons is of exceptional occurrence, *e. g.*, when chlor- and brom-benzene are conducted over strongly ignited potassium ferrocyanide, or when benzene iodide is heated to 300° with silver cyanide, the product being cyan-benzene.

Further, the nitriles of both the benzene and the paraffin series are formed when acetyl chloride or anhydride acts on the *aldoximes*:—

$$C_6H_5.CH{:}N.OH = C_6H_5.CN + H_2O.$$

The methods of formation peculiar to the benzonitriles are:—

1. The distillation of aromatic acids with potassium sulphocyanide, or what is better, with lead sulphocyanide (*Berichte*, 17, 1766):—

$$2C_6H_5.CO_2H + (CNS)_2Pb = 2C_6H_5.CN + PbS + 2CO_2 + H_2S.$$

2. To heat the phenyl mustard oils with copper, free of cuprous oxide, or with zinc dust:—

$$C_6H_5.N{:}CS + Cu = C_6H_5.CN + CuS.$$

The mustard oils can be easily obtained from the anilines, and in this manner there occurs a successive conversion of the anilines into nitriles and acids (p. 613).

When the diphenylthiureas (p. 616) are heated with zinc dust, both nitriles and anilines are produced (*Berichte*, 15, 2508):—

$$CS(NH.C_6H_5)_2 + Zn = C_6H_5.CN + C_6H_5.NH_2 + ZnS.$$

3. The distillation of the formanilides (p. 606) with concentrated hydrochloric acid or with zinc dust (*Berichte*, 17, 73):—

$$C_6H_5.NH.CHO = C_6H_5.CN + H_2O.$$

Both reactions generally yield but a small outcome, inasmuch as decompositions usually result (*Berichte*, 18, 1001).

4. The distillation of the triphenyl phosphates (p. 670) with potassium cyanide or ferrocyanide (*Berichte*, 16, 1771):—

$$PO(O.C_6H_5)_3 + 3KCN = PO(OK)_3 + 3C_6H_5.CN.$$

5. The transformation of the isomeric nitriles or carbylamines (p. 613) through the agency of strong heat:—

$$C_6H_5.NC \text{ yields } C_6H_5.CN.$$

6. The transformation of diazochlorides upon heating them with potassium cyanide and copper sulphate:—

$$C_6H_5.N_2Cl + CNK = C_6H_5.CN + KCl + N_2.$$

In this way the three nitroanilines, after conversion into diazochlorides, have been changed to the corresponding nitrobenzene nitriles, $C_6H_4(NO_2).CN$.

The benzonitriles are similar to those of the fatty series, and like them, when acted upon by alkalies or acids, form the corresponding aromatic acids. Nascent hydrogen (better sodium in alcoholic solution, p. 283) converts them into amines. They combine with alcohols and HCl, with hydroxylamine and with anilines, to form HCl-imido-ethers, oximido-ethers and benzenyl amidines (p. 735).

Benzonitrile, $C_6H_5.CN$, Cyanbenzene, is isomeric with phenyl carbylamine, $C_6H_5.NC$ (p. 613), and is best obtained from benzene sulphonic acid, by distillation with potassium cyanide, or by distilling benzoic acid with lead sulphocyanide (*Berichte*, 17, 2767). It is an oil with an odor resembling that of oil of bitter-almonds, and boils at 191°; its specific gravity = 1.023 at 0°. Like all nitriles it unites with the halogens, the halogen hydrides, and hydrogen. Acids and alkalies saponify it to benzoic acid.

Substituted benzonitriles have been obtained from the substituted benzamines.

The *nitrobenzonitriles*, $C_6H_4(NO_2).CN$, are obtained from the three nitro-anilines by diazotizing and then boiling with potassium cyanide and copper sulphate (see above). The chief product in the nitration of benzonitrile is *m*-nitrobenzonitrile, melting at 115–117°. The *ortho* melts at 109°, and the *para* at 147°. When saponified with sodium hydroxide, they yield the three nitrobenzoic acids.

Polymeric nitriles, or tricyanides, derivatives of hypothetical cyanuric acid, $C_3N_3H_3$ (p. 285), containing one alkyl and two phenyl groups, are produced when $AlCl_3$ acts upon a mixture of benzonitriles and the nitriles of fatty acids (*Berichte*, 22, 803). The hydrogen tricyanide, $C_3N_3H_3$ (p. 285), which is their basis, is a "six-membered ring," containing three C-atoms and four N-atoms. It may be considered an analogue of the pyridine, C_5H_5N, and pyrimidine, $C_4H_4N_2$, rings, each of which contain nitrogen. The derivatives of tricyanogen are, however, more easily decomposed into ammonia and the constituent acids than the last-named compounds.

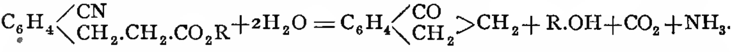
Methyldiphenyl Tricyanide, $C_3N_3(C_6H_5)_2.CH_3$, from benzonitrile with acetyl chloride and $AlCl_3$, melts at 110°. It forms salts with one equivalent of acids. **Ethyldiphenyl Tricyanide**, $C_3N_3(C_6H_5)_2.C_2H_5$, from benzonitrile and propionyl chloride, melts at 67°.

Diphenyl Tricyan Carboxylic Acid, $C_3N_3(C_6H_5)_2.CO_2H$, is formed when methyl-diphenyl cyanide is oxidized with potassium permanganate. It melts at 192°, when it decomposes into CO_2 and diphenyl tricyanogen hydride, $C_3H_3(C_6H_5)_2H$, melting at 75° (*Berichte*, 23, 2382).

Triphenyl Tricyanide, $(C_6H_5.CN)_3 = C_{21}H_{15}N_3$, **Cyanphenine**, is formed by polymerization of benzonitrile on dissolving it in fuming sulphuric acid, or boiling it with sodium, as well as by the action of sodium upon a mixture of cyanuric chloride and benzene iodide (*Berichte* 20, Ref. 102; 22, 1760), and upon heating benzylidene-benzamidine, $C_6H_5.C(NH).N:CH.C_6H_5$ (p. 736) beyond its point of fusion. It is said to be most readily obtained from benzimido ether (p. 735) (*Berichte*, 22, 1611). Cyanphenine is almost insoluble in water, alcohol and ether, readily soluble in carbon disulphide, and crystallizes in needles, melting at 231°. Nascent hydrogen converts it into ammonia and lophine, $C_{21}H_{16}N_2$. It is decomposed into ammonia and benzoic acid when it is heated with hydriodic acid.

(2) **Cyantoluenes**, $C_6H_4\begin{smallmatrix}\diagup CH_3\\ \diagdown CN\end{smallmatrix}$, Tolunitriles. The three isomerides result from the three corresponding toluidines by their conversion into mustard oils, and then heating with copper (see above), or more easily by boiling their diazo-derivatives with potassium cyanide and copper sulphate. The ortho- and para-bodies are also obtained from the toluene sulphonic acids. The *ortho* boils at 204° (*Berichte*, 19, 756); the *meta* has not yet been prepared in pure form; the *para* crystallizes in needles, melts at 28.5°, and boils at 218°. They change to the corresponding toluic acids when saponified.

o-**Cyanbenzyl Chloride**, $C_6H_4(CN).CH_2Cl$, formed by the chlorination of *o*-cyantoluene, melts at 61°, and boils at 252° (*Berichte*, 20, 2223). Aceto-acetic ester or malonic ester converts it into *o*-cyanbenzyl acetic ester. If the latter be saponified with hydrochloric acid, it will part with carbon dioxide and change to *hydrindone* (*Berichte*, 22, 2019; 23, 2479):—



$$C_6H_4\begin{smallmatrix}\diagup CN\\ \diagdown CH_2.CH_2.CO_2R\end{smallmatrix} + 2H_2O = C_6H_4\begin{smallmatrix}\diagup CO\\ \diagdown CH_2\end{smallmatrix}\!\!>CH_2 + R.OH + CO_2 + NH_3.$$

p-**Cyanbenzyl Chloride**, $C_6H_4(CN).CH_2Cl$, from *p*-cyanbenzyl toluene, melts at 79°, and boils at 263°. Potassium cyanide converts it into *p*-cyanbenzyl cyanide, which yields homoterephthalic acid (*Berichte*, 22, 3208; 23, 1059).

(3) **Benzyl Cyanide**, $C_6H_5.CH_2.CN$, is isomeric with the cyan-toluenes. This is the chief ingredient of several cresses, and is artificially prepared from benzyl chloride, $C_6H_5.CH_2Cl$, with potassium cyanide (*Berichte*, 19, 1950). It boils at 229°, and yields toluic acid by saponification.

The hydrogen of the CH_2-group, combined with the negative groups, C_6H_5 and CN, is very readily replaced (*Berichte*, 20, 534; 21, 1291). Nitrous acid, acting upon a sodium-ethylate solution of benzyl cyanide, produces isonitrosobenzyl cyanide, $C_6H_5.C(N.OH).CN$, melting at 129°. It dissolves with a yellow color in the alkalies. It forms isonitrosophenylacetic acid by saponification (*Berichte*, 22, Ref. 200). Sodium ethylate, acting upon benzyl cyanide and aldehydes, produces condensation products, *e.g.*, benzaldehyde yields α-phenyl-cinnamic nitrile, $C_6H_5.C(CH.C_6H_5)CN$. Anisic aldehyde, furfurol, etc., react similarly. The alkylic benzyl cyanides are not capable of yielding such products (*Berichte*, 21, 356; 22, Ref. 199).

One hydrogen atom of the CH_2-group can be replaced by alkyls when sodium ethylate and alkyl iodides act upon benzyl cyanide. Powdered caustic soda is frequently substituted for the sodium ethylate (*Berichte*, 21, 1291; 21, Ref. 197). In the resulting mono-alkylic benzyl cyanides, $C_6H_5.CHR.CN$, the ease with which the second H-atom can be replaced will be dependent upon the molecular magnitude and the negative character of the first substituent (*Berichte*, 22, 1238; 23, 2070).

The nitration of benzyl cyanide affords chiefly *p*-**Nitrobenzyl cyanide,** $C_6H_4(NO_2).CH_2.CN$, and slight quantities of the *o*- and *m*-bodies (*Berichte*, 17, 505); the latter can also be made from *o*- and *m*-nitrobenzalcohol by means of the chloride (*Berichte*, 19, 2636). The *ortho* crystallizes in needles from hot water and melts at 83°. The *meta* melts at 61°, and the *para* at 114°. Alcoholic soda dissolves the *ortho* with a violet color, the *para* with a carmine red color, forming salts of the alkali metals, in which the metal may be replaced by radicals (*Berichte*, 21, 2477; 22, 327). Diazobenzene chloride and the *para* compound yield an azo- and a hydrazo-derivative. They yield condensation products with the aldehydes (*Berichte*, 23, 3133). The **Amidobenzyl Cyanides,** $C_6H_4(NH_2).CH_2.CN$, result from the reduction of the nitrobenzyl cyanides with tin and hydrochloric acid. When diazotized, the para- and meta-compounds yield **oxybenzyl cyanides,** $C_6H_4.(OH).CH_2.CN$, which further form oxyphenyl acetic acids, $C_6H_4(OH).CH_2.CO_2H$.

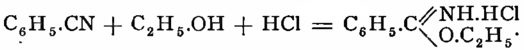
(4) **Dicyanbenzenes,** $C_6H_4(CN)_2$, result from the three brombenzene sulphonic acids, and on distilling the benzene-disulphonic acids with potassium cyanide. The *meta-body* (also obtained from isophthalamide), melts at 156°; the para- at 220°; the former yields isophthalic and the latter terephthalic acid.

(5) **Tolyl Cyanides,** $C_6H_4(CH_3).CH_2.CN$. The three isomerides have been obtained from the three xylenes by means of the tolyl bromides, $C_6H_4(CH_3).CH_2Br$. The CH_2-group in these compounds can be readily replaced (*Berichte*, 21, 1331).

(6) **Xylylene Cyanides,** $C_6H_4(CH_2.CN)_2$, have been obtained from the corresponding bromides. Both CH_2-groups in them are easily substituted (*Berichte*, 21, 72, 2318).

In this connection may be mentioned the *imido-ethers* and *oximido-ethers*, also the *benzenylamidines* and *benzenyloxamidines*.

The *imido-ethers* (their HCl-salts) result from the action of HCl upon a mixture of a benzonitrile with an alcohol (p. 292):—

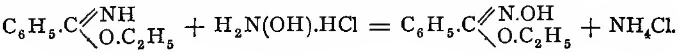


$$C_6H_5.CN + C_2H_5.OH + HCl = C_6H_5.C\begin{array}{l}\diagup NH.HCl\\ \diagdown O.C_2H_5.\end{array}$$

All cyanides react in a like manner (*Berichte*, 21, 2650), with the exception of those in which an ortho-position, relatively to cyanogen, is replaced by a C-group; therefore, in the case of the *o*-dicyanides, only one cyanogen group reacts (*Berichte*, 23, 2917). Water decomposes the HCl-imido-ethers into acid esters and ammonium chloride. For the action of secondary amines, consult *Berichte*, 23, 2927.

Benzimido-Ethyl Ether, $C_6H_5.C(NH).O.C_2H_5$, is formed by the action of ethyl iodide upon silver benzamide. Its hydrochloric acid salt consists of large, shining prisms, and at 120° decomposes into benzamide and ethyl chloride. The free ether, separated by alcoholic ammonia, is a thick oil, which decomposes when heated or when standing into alcohol and cyanphenine.

The *oximido ethers*, or *acidoximes* result when hydroxylamine acts on the imido-ethers (p. 292):—



$$C_6H_5.C\begin{array}{l}\diagup NH\\ \diagdown O.C_2H_5\end{array} + H_2N(OH).HCl = C_6H_5.C\begin{array}{l}\diagup N.OH\\ \diagdown O.C_2H_5\end{array} + NH_4Cl.$$

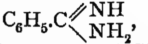
Benzoximido-ether, $C_6H_5.C(N.OH).O.C_2H_6$, is a liquid, dissolving in ether, and solidifying to a crystalline mass. It is identical with the so-called **Ethyl-benzo-hydroxamic Acid** (*Berichte*, 17, 1587), obtained from benzoyl chloride and hydroxylamine.

The benzenylamidines, or benzamidines, correspond perfectly to the amidines of the paraffin series (p. 293), also to the ethenyl-diphenyl-amidines, and the phenylene-amidines or anhydro bases (p. 627).

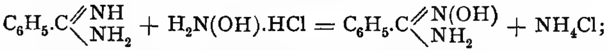
Phenylcyanate (p. 613) converts the amidines into diureïdes, *e. g.*,

$$C_6H_5.C\genfrac{}{}{0pt}{}{/\!\!/ N.CO.NH.C_6H_5}{\diagdown NH.CO.NH.C_6H_5}$$

(*Berichte*, 23, 2923), while if phenyl mustard oil be employed the products will be *amidine thioureas*, $C_6H_5.C(NH).NH.CS.NH.C_6H_6$ (*Berichte*, 22, 1609). Acid anhydrides convert them into *acidyl amidines*, *e. g.*, benzoyl benzamidine, $C_6H_5.C(NH)NH.CO.\ C_6H_5$ (*Berichte*, 22, 1605). The amidines combine with aldehydes to *alkylidene amidines*, *e. g.*, benzylidene amidine, $C_6H_5.C(NH).N:CH.C_6H_5$ (*Berichte*, 22, 1610; 23, 2924). β-Ketonic esters, as acetoacetic esters, etc., cause the amidines to condense to *oxypyrimidines*. Succino-succinic ester produces keto-quinazolines (*Berichte*, 23, 2623). See *Berichte*, 23, 2934 for the action of aromatic a-oxycarboxylic acids.

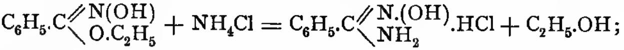
Benzenylamidine,  $C_6H_5.C\genfrac{}{}{0pt}{}{/\!\!/ NH}{\diagdown NH_2}$, *Benzamidine*. Its hydrochloride is formed when alcoholic ammonia acts upon HCl-benzimido-butyl ether (p. 292.) It consists of large vitreous crystals containing two molecules of water and melts at 72°. When anhydrous it melts at 169° (*Berichte*, 22, 1607). The free benzenylamidine, separated by sodium hydroxide, is crystalline, melts at 75–80°, and at higher temperatures breaks up into $3NH_3$ and cyanphenine. *Benzylidene Benzamidine* (see above) melts at 152°, and readily yields cyanphenine. Nitrous acid converts it into the dinitroso-compound, $C_7H_5.N_2H(NO)_2$. **Phenylbenzenylamidine**,  $C_6H_5.C\genfrac{}{}{0pt}{}{/\!\!/ NH}{\diagdown NH.C_6H_5}$, results from benzonitrile or thiobenzamide, $C_6H_5.CS.NH_2$, when heated with aniline hydrochloride (p. 293). It melts at 112°, and when distilled yields benzonitrile and aniline. Symmetrical **Diphenyl-benzenyl-amidine**, $C_6H_5.C(N.C_6H_5).NH.C_6H_5$, obtained from benzanilide, $C_6H_5.CO.NH.C_6H_5$, or benzotrichloride, $C_6H_5.CCl_3$, by means of aniline hydrochloride, melts at 144°. Unsymmetrical $C_6H_5.C(NH).N(C_6H_5)_2$, from benzonitrile and diphenylamine, melts at 111° (*Annalen*, 192, 4).

The *Oxamidines* or *Amidoximes* are produced: 1, by the action of hydroxylamine hydrochloride upon the benzenylamidines:—



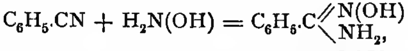
$$C_6H_5.C\genfrac{}{}{0pt}{}{/\!\!/ NH}{\diagdown NH_2} + H_2N(OH).HCl = C_6H_5.C\genfrac{}{}{0pt}{}{/\!\!/ N(OH)}{\diagdown NH_2} + NH_4Cl;$$

2, by the action of the same reagent upon the imido-ethers, when the ammonium chloride very likely acts on the oximido-ethers first formed (*Berichte*, 17, 1588 and 1694):—

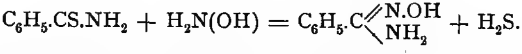


$$C_6H_5.C\genfrac{}{}{0pt}{}{/\!\!/ N(OH)}{\diagdown O.C_2H_5} + NH_4Cl = C_6H_5.C\genfrac{}{}{0pt}{}{/\!\!/ N.(OH)}{\diagdown NH_2}.HCl + C_2H_5.OH;$$

3, from the nitriles and thioamides by direct union with hydroxylamine (*Berichte*, 19, 1669):—



$$C_6H_5.CN + H_2N(OH) = C_6H_6.C\genfrac{}{}{0pt}{}{/\!\!/ N(OH)}{\diagdown NH_2,}$$

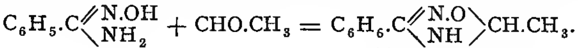


$$C_6H_5.CS.NH_2 + H_2N(OH) = C_6H_5.C\genfrac{}{}{0pt}{}{/\!\!/ N.OH}{\diagdown NH_2} + H_2S.$$

Ferric chloride imparts a deep red color to the alcoholic solution of the amidoximes.

Benzenylamidoxime, $C_6H_5.C\left\langle\begin{matrix}N(OH)\\ NH_2\end{matrix}\right.$ (*Berichte,* 18, 1053), crystallizes from ether in large plates, and melts at 79–80°. It gives the isonitrile reaction with chloroform and potassium hydroxide. Nitrous acid changes it to benzamide, $C_6H_5.CO.NH_2$. With acids and caustic alkalies it yields salts, *e.g.,* $C_6H_5.C(N.OH)NH_2.HCl$ and $C_6H_6.C(NH_2):N.OK$. Alkylic iodides convert the latter into amidoxime-ethers, *e.g.,* $C_6H_5.C(NH_2):N(O.C_2H_6)$, which nitrous acid changes to ethers of *benzhydroximic acid,* $C_6H_6.C\left\langle\begin{matrix}N(OR)\\ OH\end{matrix}\right.$. Tiemann (*Berichte,* 18, 727) considers these ethers different from those of benzhydroxamic acid (p. 746) while according to Lossen they are identical (*Berichte,* 22, Ref. 588).

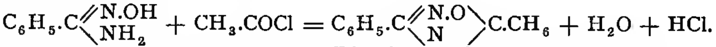
The amidoximes condense with the aldehydes to *hydrazoximes* (*Berichte,* 22, 2412, 3140):—



$$C_6H_5.C\left\langle\begin{matrix}N.OH\\ NH_2\end{matrix}\right. + CHO.CH_3 = C_6H_6.C\left\langle\begin{matrix}N.O\\ NH\end{matrix}\right\rangle CH.CH_3.$$

Ethylidene Benzenyl-hydrazoxime.

Azoximes, *e.g.,* benzenylazoxime, $C_6H_5.C\left\langle\begin{matrix}NO\\ N\end{matrix}\right\rangle C.R$ (*Berichte,* 22, 2758; 19, 1475), result from the action of chlorides or anhydrides of organic acids upon the amidoximes:—



$$C_6H_5.C\left\langle\begin{matrix}N.OH\\ NH_2\end{matrix}\right. + CH_3.COCl = C_6H_5.C\left\langle\begin{matrix}N.O\\ N\end{matrix}\right\rangle C.CH_6 + H_2O + HCl.$$

Ethenyl Benzenylazoxime.

They are also produced by the oxidation of the hydrazoximes (see above).

ACIDS.

The aromatic acids are derived by replacing hydrogen in the benzenes by carboxyls:—

$C_6H_5.CO_2H$ Benzoic Acid.

$C_6H_4\left\{\begin{matrix}CH_3\\ CO_2H\end{matrix}\right.$ Toluic Acids.

$C_6H_3\left\{\begin{matrix}(CH_3)_2\\ CO_2H\end{matrix}\right.$ Xylic Acids.

$C_6H_5.CH_2.CO_2H$ Alphatoluic Acid or Phenylacetic Acid.

$C_6H_5.CH_2.CH_2.CO_2H.$ Hydrocinnamic or β-Phenylpropionic Acid.

$C_6H_4\left\{\begin{matrix}CO_2H\\ CO_2H\end{matrix}\right.$ Benzene Dicarboxylic Acids.

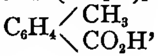
$C_6H_3(CO_2H)_3$ Benzene Tricarboxylic Acids.

$C_6H_2(CO_2H)_4$ Benzene Tetracarboxylic Acids.

$C_6(CO_2H)_6.$ Mellitic Acid.

The important general methods of forming the aromatic acids are:—

1. The oxidation of the hydrocarbons with a chromic acid mixture, potassium permanganate or dilute nitric acid. The side-chains are directly converted, by chromic acid, into CO_2H; the hydrocarbons, $C_6H_5.CH_3$, $C_6H_5.C_2H_5$, $C_6H_5.C_3H_7$, etc., all yield benzoic acid, $C_6H_5.CO_2H$. With nitric acid it is sometimes possible to oxidize only the most extreme carbon atom of the side-chain.

Should several side-chains chance to be present, chromic acid will almost invariably oxidize them all directly to CO_2H. Thus, the xylenes, $C_6H_4(CH_3)_2$, yield dicarboxylic acids, $C_6H_4\,(CO_2H)_2$. Dilute nitric acid forms mono-carboxylic acids, *e.g.*,  $C_6H_4\begin{cases} CH_3 \\ CO_2H \end{cases}$, and potassium permanganate produces both varieties.

Only the *para-* and *meta-derivatives* (the former more readily than the latter) of benzenes, carrying two side-chains (the xylenes and toluic acids), are oxidized to acids by chromic acid, while the ortho- are either not attacked at all or are completely destroyed. Nitric acid, or better, potassium permanganate, oxidizes all (even the ortho-derivatives) to their corresponding acids. The haloid toluenes (p. 584), the nitro-toluenes (p. 590), and toluene sulphonic acids (p. 665) deport themselves similarly. The same is observed with dialkyl benzenes, where the entrance of a negative group hinders the oxidation of the alkyl occupying the ortho- place (*Berichte*, 15, 1022).

In the homologous phenols the OH-group completely prevents the oxidation of the alkyls by the oxidizing agents mentioned; this is true, too, in all the isomerides; but it does occur in a peculiar manner, if the phenyl hydrogen be replaced by alkylic groups or acid radicals (p. 686).

In the derivatives with two different alkyls (*e.g.*, cymene, $C_6H_4(CH_3).(C_3.H_7)$, the higher alkyl is usually attacked first, by nitric acid or chromic acid (or CrO_2Cl_2), and converted into carboxyl (*Berichte*, 11, 619); while in the animal organism the methyl group suffers oxidation (*Berichte*, 16, 619). Sometimes, however, the methyl group is first oxidized; this occurs when dilute nitric acid is the oxidizing agent (*Berichte*, 19, 1728). Potassium permanganate occasions at first an entrance of OH in the propyl group, accompanied often by a transposition (p. 346 and *Berichte*, 14, 1135).

Potassium ferricyanide oxidizes methyl to carboxyl, if the nitro-group occupies the ortho position relatively to the methyl group. This does not occur if the nitro-group holds the meta-position (*Berichte*, 22, Ref. 201, 501).

In oxidizing the benzenes with chromic acid it is customary to employ a mixture of $Cr_2O_7K_2$ (2 parts) with sulphuric acid (3 parts), which is diluted with 2–3 volumes of H_2O, and apply it in the quantity necessary for oxidation ($Cr_2O_7K_2$ yields 3O and oxidizes $1CH_3$). The mixing is performed in a flask provided with a long upright tube, the whole boiled for some time, until all the chromic acid is reduced and the solution has acquired a pure green color. The product is diluted with water, the solid acid filtered off and purified by dissolving in soda, etc. Soluble acids are extracted with ether; the volatile acids are distilled over with steam.

When oxidizing with nitric acid, use acid diluted with 3 parts of water and boil for some time, in connection with a return condenser (2–3 days). To remove the nitro-acids which are invariably formed, the crude product is digested with tin and concentrated hydrochloric acid; this converts the nitro- into amido-acids, which dissolve in hydrochloric acid.

Potassium permanganate often effects the oxidation at ordinary temperatures. The substance or (with acids) its alkaline solution, is shaken with an excess of permanganate; hydrated manganese dioxide separates, while the potassium salt of the acid produced passes into the solution.

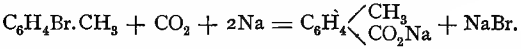
2. Oxidation of the aromatic aldehydes and alcohols.

3. The conversion of the nitriles (p. 211) when boiled with alkalies or acids:—

$$C_6H_5.CN + 2H_2O = C_6H_6.CO_2H + NH_3,$$
$$C_6H_5.CH_2.CN + 2H_2O = C_6H_6.CH_2.CO_2H + NH_3.$$

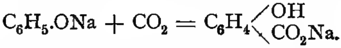
Hydrochloric acid changes the oxychlorides (obtained from the aldehydes and ketones with CNH) to oxy-acids (p. 347). Sometimes in this case chlorinated acids first form, and are converted into oxy-acids by boiling with alkalies (see Mandelic acid).

4. Action of sodium and CO_2 upon mono-brombenzenes—*Kekulè*:—



$$C_6H_4Br.CH_3 + CO_2 + 2Na = C_6H_4\left\langle\begin{matrix}CH_3\\CO_2Na\end{matrix}\right. + NaBr.$$

The phenols react directly with CO_2 and sodium, forming oxy-acids—*Kolbe*:—



$$C_6H_5.ONa + CO_2 = C_6H_4\left\langle\begin{matrix}OH\\CO_2Na.\end{matrix}\right.$$

Instead of letting sodium and carbon dioxide act on the free phenols, it is better to expose the alkaline phenates to heat, in a current of CO_2-gas (see Salicylic Acid). If the CO_2 should act further above 300°, oxyisophthalic acid and oxytrimesic acid will result. In the substituted phenols (their ethers) the halogen atom is replaced by the carboxyl-group:—

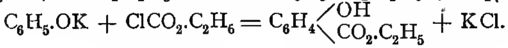
$$C_6H_4Br.O.CH_3 + CO_2 + 2Na = C_6H_4(O.CH_3).CO_2Na + NaBr.$$

The dioxyphenols of the meta-series (resorcinol, orcinol) can be changed to dioxyacids when heated with ammonium carbonate or potassium (sodium) dicarbonate and water to 130°, or even by merely boiling them (*Berichte*, 18, 3202; 19, 2318):—

$$C_6H_4(OH)_2 + CO_2 = C_6H_3(OH)_2.CO_2H.$$

5. A similar reaction is that of sodium and esters of chlorcarbonic acid upon phenols and brom-hydrocarbons—*Würtz*:—

$$C_6H_5Br + ClCO_2.C_2H_5 + 2Na = C_6H_5.CO_2.C_2H_6 + Na_2(BrCl),$$



$$C_6H_5.OK + ClCO_2.C_2H_6 = C_6H_4\left\langle\begin{matrix}OH\\CO_2.C_2H_5\end{matrix}\right. + KCl.$$

6. The action of phosgene gas upon benzene in the presence of $AlCl_3$ (p. 569); at first acid chlorides are produced, and these change further into benzene-ketones:—

$$C_6H_6 + COCl_2 = C_6H_5.COCl + HCl.$$

Similarly, phosgene and esters of chloroxalic acid act directly upon dimethyl aniline (p. 601).

Ethyl urea chloride, in the presence of $AlCl_3$, acts in an analogous manner upon benzenes—the products then are derivatives of aromatic acids (*Berichte*, 20, 120):—

$$C_6H_6 + Cl.CO.NH.C_2H_5 = \underset{\text{Ethylbenzamide.}}{C_6H_5.CO.NH.C_2H_5} + HCl;$$

urea chloride, $Cl.CO.NH_2$ (p. 376) behaves similarly (*Berichte*, 21, Ref. 294):—

$$C_6H_5 + Cl.CO.NH_2 = \underset{\text{Benzamide.}}{C_6H_5.CO.NH_2} + HCl;$$

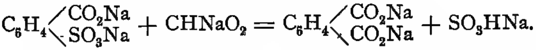
while diphenylurea chloride $(C_6H_5)_2.N.CO.Cl$ (p. 611) (*Berichte*, 20, 2118) and phenylisocyanate (carbanile) (*Berichte*, 18, 873, 2338) may be included in the same category:—

$$C_6H_6 + CO.N.C_6H_5 = C_6H_5.CO.NH.\ C_6H_5.$$

A modification of the urea chloride process consists in the action of nascent cyanic acid, CONH, the benzene or phenol ether being heated with cyanuric acid $(CONH)_3$ and $AlCl_3$ (*Berichte*, 23, 1190):—

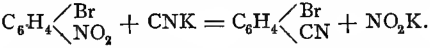
$$C_6H_6 + CONH = \underset{\text{Benzamide.}}{C_6H_5.CO.NH_2}.$$

7. Fusion of salts of sulphonic acids of the hydrocarbons, or of the aromatic acids with sodium formate:—



$$C_6H_4\begin{matrix}\diagup CO_2Na\\ \diagdown SO_3Na\end{matrix} + CHNaO_2 = C_6H_4\begin{matrix}\diagup CO_2Na\\ \diagdown CO_2Na\end{matrix} + SO_3HNa.$$

8. By heating the halogen nitro-derivatives of the hydrocarbons with potassium cyanide and alcohol, to 200–230° in sealed tubes:—

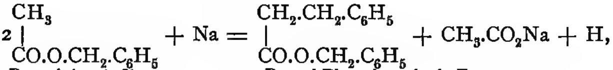


$$C_6H_4\begin{matrix}\diagup Br\\ \diagdown NO_2\end{matrix} + CNK = C_6H_4\begin{matrix}\diagup Br\\ \diagdown CN\end{matrix} + NO_2K.$$

The nitrile immediately becomes an acid. In this reaction the cyanogen group displaces NO_2, but does not assume the same position in the benzene nucleus (*Berichte*, 8, 1418). In the same manner, when alcoholic potassium cyanide acts upon *m*- and *p*-dinitrobenzene *one* nitro group is replaced by CN, while an *oxy-alkyl* group enters at the same time.

9. Action of benzyl chloride upon ethers of sodium acetoacetic ester, and the decomposition of the ketonic esters, formed at first, by alkalies (p. 212). Benzyl malonic acid, $C_6H_5.CH_2.CH(CO_2H)_2$, is similarly formed from sodium malonic ester; it loses CO_2 and becomes benzyl acetic acid, $C_6H_5.CH_2.CH_2.CO_2H$ (p. 212).

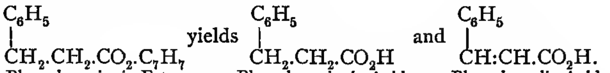
10. Action of sodium upon the benzyl esters of the fatty acids; here, too, esters are produced at first:—



$$2\begin{array}{l}CH_3\\ |\\ CO.O.CH_2.C_6H_5\end{array} + Na = \begin{array}{l}CH_2.CH_2.C_6H_5\\ |\\ CO.O.CH_2.C_6H_5\end{array} + CH_3.CO_2Na + H,$$

Benzyl Acetic Ester. Benzyl Phenylpropionic Ester.

but subsequently they yield saturated and unsaturated acids (*Annalen*, 193, 321, and **204**, 200):—



$$\begin{matrix} C_6H_5 \\ | \\ CH_2.CH_2.CO_2.C_7H_7 \end{matrix} \text{ yields } \begin{matrix} C_6H_5 \\ | \\ CH_2.CH_2.CO_2H \end{matrix} \text{ and } \begin{matrix} C_6H_5 \\ | \\ CH{:}CH.CO_2H. \end{matrix}$$

Phenylpropionic Ester. Phenylpropionic Acid. Phenylacrylic Acid.

Phenyl butyric and phenyl crotonic acids are similarly obtained from the benzyl propionic esters.

11. The direct syntheses of aromatic acids from paraffin compounds have been given upon pp. 565, 566.

12. The special synthetic methods for *oxy-acids* and *ketonic acids*, as well as for the unsaturated acids, are described under these general headings.

The aromatic acids occur naturally, partly in a free state, partly in many resins and balsams, and in the animal organism (hippuric acid, tyrosine). They arise also in the decay of albuminoid bodies (*Berichte*, 16, 2313).

The aromatic acids are crystalline solids, which generally sublime undecomposed. Most of them dissolve with difficulty in water, hence are precipitated from their salt solutions by mineral acids. Sodium amalgam or zinc dust will reduce some to aldehydes, and heating with concentrated hydriodic acid or phosphonium iodide converts them into hydrocarbons. When heated with lime or soda-lime, their carboxyl-groups are eliminated and hydrocarbons result:—

$$C_6H_4\begin{cases} CH_3 \\ CO_2H \end{cases} = C_6H_5.CH_3 + CO_2,$$
$$C_6(CO_2H)_6 = C_6H_6 + 6CO_2.$$

From the polycarboxylic acids we obtain, as intermediate products, acids having fewer carboxyl-groups, *e.g.*, phthalic acid first yields benzoic acid and then benzene:—

$$C_6H_4(CO_2H)_2 = C_6H_5.CO_2H \text{ and } C_6H_6.$$

The hydrogen of the benzene nucleus in the acids can sustain substitutions similar to those observed with the hydrocarbons and phenols. In other respects they are very similar to the fatty acids, and afford corresponding derivatives.

MONOBASIC ACIDS.

Benzoic Acid, $C_7H_6O_2 = C_6H_5.CO_2H$, occurs free in some resins, chiefly in gum benzoïn (from *Styrax benzoïn*), and in coal tar (*Berichte* **18**, 615); as hippuric acid in the urine of herbivorous animals. In addition to the general synthetic methods it is obtained from benzotrichloride, $C_6H_5.CCl_3$, when heated with water to 150°, or by mixing with sulphuric acid; also by boiling benzyl chloride, $C_6H_5.CH_2Cl$, with dilute nitric acid, or by acting on benzene with carbon dioxide in the presence of aluminium chloride.

Preparation.—Gum benzoïn is sublimed in an iron pan, covered with a paper cone. Or the powdered resin is boiled with milk of lime, lime water (to decolorize the dye stuffs) added to the filtered solution of the lime salt, and the benzoic acid precipitated with hydrochloric acid. A more advantageous method is the production of the acid from hippuric acid (benzoyl glycocoll, p. 744). To accomplish this, boil the latter for an hour with 4 parts of concentrated hydrochloric acid, and filter off the separated benzoic acid. Benzoic acid results from phthalic acid by heating its calcium salt to 300-350° (see above) with 1 molecule of calcium hydroxide.

Benzoic acid crystallizes in white, shining needles or leaflets, melts at 120°, and distils at 250°. It volatilizes readily, and is carried over with steam. It dissolves with difficulty in cold water (1 part in 600 parts), but readily when heated. The vapors possess a peculiar odor, which produces coughing.

The acid yields benzene and carbon dioxide when heated with lime; with excess of the latter benzophenone also results. Sodium amalgam converts it into benzaldehyde, hydrobenzoïn and hydrobenzoic acid, $C_7H_{10}O_2$.

The *benzoates* are mostly quite readily soluble in water. Ferric chloride throws out a reddish precipitate of ferric benzoate from their neutral solutions.

The *potassium salt*, $2C_7H_5KO_2 + H_2O$, crystallizes in concentrically grouped needles. The *calcium salt*, $(C_7H_5O_2)_2Ca + 3H_2O$, consists of shining prisms or needles. The *silver salt*, $C_7H_5AgO_2$, crystallizes from hot water in bright leaflets.

The *esters* of benzoic acid, as well as those of all other aromatic acids, are prepared by conducting hydrochloric acid into an alcoholic solution of the acid, and are aromatic-smelling liquids. They can also be obtained by shaking benzoyl chloride with alcohols and sodium hydroxide, until a permanent alkaline reaction is observed (*Berichte*, 19, 3218). The *methyl ester*, $C_7H_5O_2.CH_3$, boils at 199°, the *ethyl ester* at 213°, the *isoamyl ester* at 261°. The *isopropyl ester* boils about 218° and decomposes into benzoic acid and propylene. The *benzylic ester*, $C_6H_5.CO.O.C_7H_7$, occurs in Peru- and Tolu-balsam,* and is formed when benzyl chloride acts upon benzal alcohol. It also results from the interaction of sodium or potassium ethylate and glacial acetic acid upon benzaldehyde (benzyl

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* *Peru-* and *Tolu-balsams* are thick, yellow-brown liquids, which are obtained from the bark of varieties of *Myroxylon*. In addition to resins and some free benzoic and cinnamic acids they also contain benzyl-benzoic and cinnamic esters (Cinnameïn).

alcohol and methyl benzoic ester are also produced) (*Berichte*, 20, 647). It crystallizes in needles, melts at 21°, and boils at 324°. The *phenyl ester*, $C_6H_5.CO.O.C_6H_5$, is formed from benzoyl chloride and phenol, or by fusing benzoic acid with phenol and $POCl_3$ (p. 668); it melts at 66°.

Dihydrobenzoic Acid, $C_7H_8O_2 = C_6H_7.CO_2H$, may be prepared by oxidizing dihydrobenzaldehyde with argentic oxide (*Berichte*, 23, 2886). It does not dissolve in water as readily as benzoic acid. It volatilizes with steam, and when cooled solidifies to a feathery crystalline mass, melting at 95°. It has an odor resembling that of cinnamon, and it reduces ammoniacal silver solutions.

Hexahydrobenzoic Acid, $C_7H_{12}O_2 = C_6H_{11}.COOH$, Hexanaphthene Carboxylic Acid. This occurs together with associated acids in the petrolic acids of petroleum. It is isolated by the fractional distillation of the methyl esters (*Berichte*, 23, 870). It is a viscid oil, boiling at 215–217°. Its odor resembles that of baldrianic acid.

Benzoyl Chloride, $C_6H_5.COCl$, results when benzoic acid is distilled with PCl_5, and when chlorine acts upon boiling benzaldehyde. It is an oil with a penetrating odor. It boils at 199°, and is slowly converted into benzoic acid by water. Excess of PCl_6 converts it into benzotrichloride, $C_6H_5.CCl_3$. *Benzoyl bromide*, from benzoic acid with PBr_3, boils at 217°–220°.

Benzoyl Cyanide, $C_6H_5.CO\,CN$, is produced when benzoyl chloride is distilled with potassium or mercury cyanide. It crystallizes in large tables which melt at 34° and boil at 208°. When boiled with alkalies it changes to benzoic acid and potassium cyanide; concentrated hydrochloric acid converts it into benzoyl-formic acid. When phenylhydrazine acts upon benzoyl cyanide hydrocyanic acid is evolved and α-benzoyl phenylhydrazine results. Nitrobenzoyl cyanide (*Berichte*, 22, 329) reacts in a similar manner.

Benzoic Anhydride, $(C_7H_5O)_2O$, is obtained by heating dry sodium benzoate (6 parts) to 130° with PCl_3O (1 part), or upon digesting benzoyl chloride with lead nitrate (*Berichte*, 17, 1282). It consists of prisms insoluble in water, melts at 42°, and boils at 360°. It changes to the acid on boiling with water. **Benzoyl Peroxide**, $(C_7H_5O)_2O_2$, forms large crystals, melts at 100° and deflagrates.

Thiobenzoic Acid, $C_6H_5.CO.SH$, results when benzoyl chloride acts upon alcoholic potassium sulphide. It is crystalline, melts at 24° and distils in aqueous vapor. Its *ethyl ester* boils at 243°. When its ethereal solution is exposed to the air the acid rapidly changes to *Benzoyl disulphide*, $(C_7H_5O)_2S_2$; brilliant crystals, which melt at 128°. *Benzoyl sulphide*, $(C_7H_5O)_2S$, is obtained when benzoyl chloride acts upon thiobenzoic acid. It crystallizes from ether in large prisms, melts at 48° and decomposes when distilled.

Dithiobenzoic Acid, $C_6H_5.CS.SH$, is obtained when $C_6H_6.CCl_3$ is boiled with alcoholic potassium sulphide; $C_6H_5CCl_6 + 2K_2S = C_6H_5CS_2K + 3KCl$. The free acid is very unstable. The lead salt crystallizes from carbon disulphide in red needles.

Amide Derivatives of Benzoic Acid.

Benzamide, $C_6H_5.CO.NH_2$, results when benzoyl chloride or benzoic ester acts upon alcoholic ammonia. It is best obtained by heating benzoic acid and ammonium thiocyanate to 170°. It crystallizes in pearly leaflets, melts at 130°, and boils near 288°. It is readily soluble in hot water, alcohol and ether.

It combines with hydrochloric acid to $C_7H_7ON.HCl$. When it is boiled with mercuric oxide we obtain the crystalline compound $C_6H_5.CO.NHg$. **Silver benzamide**, $C_6H_5.CO.NHAg$ or $C_6H_6.C(NH).O.Ag$, obtained by precipitating the aqueous solution of benzamide and silver nitrate with sodium hydroxide, is a brown precipitate. When digested with ethyl iodide it yields benzimido-ethyl ether, $C_6H_5.C(NH).O.C_2H_5$ (p. 735) (*Berichte*, 23, 105, 1550). Consult *Berichte*, 23, 3039 for sodium benzamide.

Methylene-dibenzamide, $CH_2(NH.CO.C_6H_5)_2$, is identical with the so-called *hipparaffin* obtained in the oxidation of hippuric acid with PbO_2 and nitric acid, and results from benzonitrile and methylene dimethylate. It melts at 233° and when heated with water is decomposed into benzamide and formaldehyde.

Dibenzamide, $(C_7H_5O)_2NH$, results from the action of sulphuric acid upon benzonitrile. It melts at 148° and dissolves in sodium hydroxide to the salt $(C_7H_5O)_2N.Na$.

Thiobenzamide, $C_6H_5.CS.NH_2$, is formed when hydrogen sulphide is conducted into an ammoniacal, alcoholic solution of benzonitrile (p. 260). It melts at 116°. Hydrochloric acid and zinc convert it into benzylamine (*Berichte* 21, 53). **Thiobenzanilide**, $C_6H_5.CS.NH.C_6H_6$, may be obtained from phenyl-benzenylamidine by the action of hydrogen sulphide or carbon disulphide. It forms yellow plates, melting at 98°.

On mixing aniline and benzoyl chloride we get **Benzanilide**, $C_6H_6.CO.NH.C_6H_5$, **Phenyl-benzamide**, which can also be made by the action of aluminium chloride (p. 727) upon benzene and carbanile, and upon heating diphenyl-ketoxime, $(C_6H_5)_2C:N.OH$, whereby a molecular transposition is brought about. It crystallizes from alcohol in leaflets, melts at 158–160°, and distils without decomposition. PCl_6 converts it into **benzanilide-imidechloride**, $C_6H_6.CCl:N.C_6H_5$ (p. 258), which can also be obtained from diphenyl-ketoxime $(C_6H_6)_2C:N.OH$, by a transposition of the chloride (*Berichte*, 19, 992; 20, 504):—

$$(C_6H_5)_2C:NCl \quad \text{yields} \quad C_6H_5.CCl:N.C_6H_6.$$

From benzene the imidechloride crystallizes in large leaflets, melting at 40°, and boiling at 310°. Water or alcohol resolves it into hydrochloric acid and benzanilide.

Benzanilide-imidechloride, acting upon aceto-acetic ester or malonic ester, produces compounds like $C_6H_5.N:C(C_6H_5).CH\begin{smallmatrix}\diagup CO_2R \\ \diagdown CO_2R\end{smallmatrix}$, anil-benzenyl-malonic ester, which, when heated, eliminate alcohol, and by the closing-up of the ring yield quinoline derivatives (*Berichte*, 19, 1462).

Benzoyl Toluidines, $C_6H_5.CO.NH.C_6H_4.CH_3$, are similarly produced from the three toluidines with benzoyl chloride, and with PCl_5 yield the corresponding imidechlorides, $C_6H_5.CCl:N.C_7H_7$, which, upon further condensation with malonic esters, yield quinoline derivatives (Just, *Berichte*, 19, 979 and 1541).

Hippuric Acid, Benzoyl glycocoll, $C_9H_9NO_3 = CH_2\begin{smallmatrix}\diagup NH.CO.C_6H_5 \\ \diagdown CO_2H\end{smallmatrix}$, occurs in considerable amount in the urine of herbivorous animals, sometimes in that of man. Benzoic acid, cinnamic acid, toluene and other aromatic substances, when taken internally, are eliminated as hippuric acid. It can be obtained artificially by heating benzamide with monochloracetic acid:—

$$C_6H_5.CO.NH_2 + CH_2Cl.CO_2H = C_6H_6.CO.NH.CH_2.CO_2H + HCl,$$

by the action of benzoyl chloride on silver glycocollide (*Berichte*, **15**, 2741), or by adding sodium hydroxide to glycocoll and shaking with benzoyl chloride (*Berichte*, **19**, Ref. 307), and by heating benzoic anhydride with glycocoll (*Berichte*, **17**, 1662).

To prepare it boil the urine of horses with milk of lime, filter, concentrate the solution, and precipitate with hydrochloric acid. To purify the crude acid digest it with chlorine water, or dissolve it in dilute sodium hydroxide, add sodium hypochlorite, boil to decolorization, and then precipitate the cold solution with hydrochloric acid.

Hippuric acid crystallizes in rhombic prisms, and dissolves in 600 parts cold, and readily in hot water and alcohol. It melts at 187°, and about 240° decomposes into benzoic acid, benzonitrile and prussic acid. Phosphorus pentachloride converts it into isoquinoline, while its ethyl ester yields **Hippuroflavin**, $C_9H_5.NO_2$ (*Berichte*, **21**, 3321).

Its *silver salt*, $C_9H_8AgNO_3$, crystallizes from water in silky needles. The *ethyl ester* is best obtained by digesting glycocoll ester with benzoic anhydride; it is crystalline, melts at 60°, and decomposes when distilled.

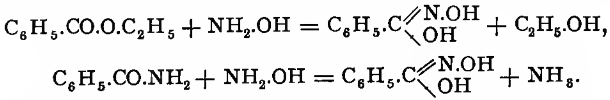
Boiling acids or alkalies decompose hippuric acid into benzoic acid and glycocoll. Nitrous acid converts it into **benzoyl glycollic Acid**, $CH_2\langle{}^{O.C_7H_5O}_{CO_2H}$, which crystallizes in fine needles. It is easily soluble in hot water, is monobasic, and yields salts which are readily soluble. Consult *Berichte*, **22**, Ref. 551, for the condensation products obtained from hippuric acid and the aldehydes.

Potassium chlorate and hydrochloric acid produce chlorinated hippuric acids. *m*-Nitrohippuric acid, $C_9H_8(NO_2)NO_3$, is obtained by adding hippuric acid to a mixture of nitric and sulphuric acids. It forms shining prisms, which are not very soluble in water, and melt about 150°. When boiled with acids it breaks up into glycocoll and *m-nitrobenzoic acid* (p. 747).

Benzoyl Hydrazine, $C_6H_5.CO.NH.NH_2$, is a derivative of diamide, N_2H_4 (p. 166). It may be prepared by the action of hydrazine upon benzoyl glycollic ester (*Berichte*, **23**, 3023). It crystallizes in large leaflets, melting at 112°. Sodium nitrite and acetic acid convert in into *Benzoyl Azimide*, $C_6H_5.CO.N{:}N_2$ (p. 640), which by boiling with sodium hydroxide, is converted into benzoic acid and the sodium salt of *azoimide* or *hydrazoic acid*, HN_3.

Benzhydroxamic Acids (p. 260).

These acids are produced in the same manner as the analogous acids of the fatty series from the acid chlorides, esters and amides, by the action of hydroxylamine (*Berichte*, **22**, 2856, 3070; Ref. 587) (see *Berichte*, **22**, 1270):—

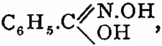


$$C_6H_5.CO.O.C_2H_5 + NH_2.OH = C_6H_5.C\langle{}^{N.OH}_{OH} + C_2H_5.OH,$$

$$C_6H_5.CO.NH_2 + NH_2.OH = C_6H_5.C\langle{}^{N.OH}_{OH} + NH_3.$$

When these are heated with phenylhydrazine the oxime-group is eliminated and oxyhydrazones result (*Berichte*, **22**, 3070):—

$$C_6H_5.C(OH).(N.OH) + NH_2.NH.C_6H_5 = C_6H_5.C(OH)(N.NH.C_6H_5) + H_2N.OH.$$

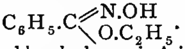
Benzhydroxamic Acid,  $C_6H_5.C\left\langle\begin{matrix}N.OH\\OH\end{matrix}\right.$, is very soluble in hot water. It crystallizes in leaflets and plates, melting at 125° (*Berichte*, 12, 1272).

Two isomeric ethers are derived from it by the introduction of alkyls:—

$$C_6H_5.C\left\langle\begin{matrix}N.O.C_2H_5\\OH\end{matrix}\right.$$

Alkyl Benzhydroxamic Ether.

and



$$C_6H_5.C\left\langle\begin{matrix}N.OH\\O.C_2H_5\end{matrix}\right..$$

Alkyl-benzhydroxamic Acid.

The first result when alkyl iodides and caustic alkali act upon benzhydroxamic acid. They are identical with the benzhydroximic acids obtained from benzenylamidoxime by alkylization and the subsequent action of nitrous acid (Lossen, *Berichte*, 22, 588). Acids resolve them into benzoic acid and *a*-hydroxylamine ethers, $H_2N.OR$ (p. 166).

The second class are produced when the benzoyl group is introduced into benzhydroxamic acid and the product further alkylized, etc. They are identical with the benzoximido-ethers prepared from benzimido-ether. When the ethyl derivative is digested with hydrochloric acid it forms ethyl chloride and benzhydroxamic acid (*Berichte*, 22, Ref. 588). The benzhydroxamic ethers and ethylbenzhydroxamic acid yield the same ethyl benzhydroxamic ethylate, $C_6H_5.C.(N.O.C_2H_5).O.C_2H_5$.

Substituted Benzoic Acids.

These are formed by the direct substitution of benzoic acid or by oxidizing substituted toluenes. The action of the halogens (or of hydrochloric acid and potassium chlorate; of bleaching lime and of antimony chloride) upon benzoic acid is not as energetic as upon the hydrocarbons; the mono-substitution products of the *meta* series (p. 589) are almost the sole products. In the action of nitric acid small quantities of ortho- and para- compounds also result. The mono-substituted toluenes of the *meta* and *para* series are readily oxidized by chromic acid to the corresponding substituted benzoic acids, whereas the ortho-derivatives are attacked with difficulty and then completely decomposed (p. 738). However, the ortho-compounds are oxidized to the corresponding benzoic acids by dilute nitric acid, or by an excess of potassium permanganate. Thus (1, 2)-brom-, iodo- and nitro-toluene yield (1, 2)-brom-, iodo- and nitrobenzoic acids. Furthermore, substituted benzoic acids can be obtained from the oxy-acids by PCl_5 and also from the amido-benzoic acids (by forming the diazo-compound and boiling with the haloid acids). When the halogen nitrobenzenes are heated with potassium cyanide substituted benzoic acids are the products. The ortho- melt at the lowest temperatures, are rather readily soluble in water, and yield easily soluble barium salts, whereby they can usually be quite readily separated from the meta- and para-derivatives. When they are fused with caustic potash oxy-acids result.

Monochlorbenzoic Acids, $C_6H_4Cl.CO_2H$. The *ortho* (1, 2)-body was formerly called chlorsalicylic acid, and may be obtained from salicylic acid, $C_6H_4(OH).CO_2H$, by the action of PCl_5; the chloride, $C_6H_4Cl.CO.Cl$, formed at first, boils at 240° and is decomposed by boiling water. It sublimes in needles, melting at 137° (they melt below 100° in water). They can also be obtained from (1, 3)-chlornitrobenzene by the action of potassium cyanide. *Metachlorbenzoic Acid* (1, 3) is produced by oxidizing (1, 3)-chlortoluene, and from benzoic acid by boiling it with hydrochloric acid and ClO_3K, with HCl and MnO_2, with bleaching lime or with $SbCl_5$; also from chlorhippuric acid, and from (1, 4)-chlornitrobenzene with potassium cyanide. It sublimes in flat needles, melting at 153°. *Parachlorbenzoic Acid* (1, 4), called chlordracrylic acid, is obtained from (1, 4)-chlortoluene; it sublimes in scales, and melts at 240°.

Monobrombenzoic Acids, $C_6H_4Br.CO_2H$. The *ortho-acid*, from orthobromtoluene (with nitric acid) and from orthoamidobenzoic acid (on heating the perbromide of the diazo-compound with alcohol), sublimes in needles and melts at 147-148°; its barium salt is very soluble in water. The *common metabrombenzoic acid*, obtained from (1, 3)-bromtoluene, and by heating benzoic acid and bromine to 120–130° (with some 1, 2-brombenzoic acid), sublimes in needles, melting at 155°. (1, 4)-*Brombenzoic Acid*, from parabromtoluene, is almost insoluble in water, crystallizes in needles, and melts at 251°.

Monoiodo-benzoic Acids, $C_6H_4I.CO_2H$. The *ortho*-acid from ortho-iodotoluene (by means of nitric acid) and ortho-amidobenzoic (by decomposition of the diazo-compound with hydriodic acid) forms needles and melts at 159°. It yields salicylic acid with caustic potash. *Metaiodobenzoic Acid* (1, 3), from meta-iodo-toluene and meta amidobenzoic acid, sublimes in needles, and melts at 187°; (1, 3)-oxybenzoic acid results when it is fused with caustic potash. *Paraiodobenzoic Acid* (1, 4), from paraiodo-toluene, paraiodo-propyl benzene, para-amidobenzoic acid and *p*-amidoacetophenone, crystallizes from alcohol in pearly leaflets, sublimes in scales and melts at 265°. When fused with potassium hydroxide it yields paraoxybenzoic acid.

Fluorbenzoic Acids, $C_6H_4Fl.CO_2H$. These are obtained by boiling the three diazoamido-benzoic acids with hydrofluoric acid. The *ortho-acid* melts at 118°, the *meta-acid* at 124°, and the *para-acid* at 181° (*Berichte*, 15, 1197). They separate out in urine as fluorhippuric acids. *Di-fluor-benzoic Acid*, $C_6H_3Fl_2.CO_2H$, from benzoic acid and Cr_2Fl_6, is in external properties very similar to benzoic acid. It melts at 232°.

Nitrobenzoic Acids, $C_6H_4(NO_2).CO_2H$.

Metanitrobenzoic acid is the principal product in the nitration of benzoic acid. The quantity of the ortho (20 per cent.) and para (1.8 per cent.) acids is less.

Preparation.—Gradually add sulphuric acid (4 parts) to a mixture of fused and pulverized benzoic acid (1 part) with nitre (2 parts) and apply heat to the mass until it melts, then pour the fused acids off from the potassium sulphate. To effect their separation convert them into barium salts and recrystallize; the barium salt of the meta-acid dissolves with great difficulty (*Annalen*, 193, 202). In the nitration of cinnamic acid *p*- and *o*-nitro-cinnamic acids are formed. The oxidation of these yields the corresponding nitrobenzoic acids. The nitration of hippuric acid gives rise to a nitrohippuric acid, which yields metanitrobenzoic acid. The nitrobenzoic acids can also be prepared by oxidizing the three nitrotoluenes (p. 746), and ortho- and para-nitrobenzyl chloride (p. 584) with potassium permanganate; further, by converting the three nitroanilines into three nitrobenzonitriles and saponifying the latter with alkalies (p. 634) (*Berichte*, 18, 1492). The *ortho*-acid is most easily prepared by oxidizing *o*-nitrotoluene with potassium permanganate (*Berichte*, 12, 443) and the *para*-acid by oxidizing *p*-nitrotoluene with a chromic acid mixture.

(1, 2)-*Nitrobenzoic Acid* crystallizes in needles or prisms, melts at 147°, possesses a sweet taste and dissolves in 164 parts of water at 16°. In the action of PCl_5 upon it there is formed, in addition to *o*-nitrobenzoyl chloride, the anhydride of *o*-nitrobenzoic acid, $(C_6H_4(NO_2)CO)_2O$, melting at 135° (*Berichte*, 17, 2789). The ordinary (1, 3)-*nitrobenzoic acid* crystallizes in needles or leaflets, sublimes in white needles and melts at 142°. After slow cooling it melts at 135–136° and dissolves in 425 parts of water at 16.5°. (1, 4)-*Nitrobenzoic acid*, also obtained by oxidizing para-nitrotoluene, forms yellowish leaflets, melts at 240° and dissolves with difficulty in water.

When the (1, 3)-brombenzoic acid is nitrated two nitrobrombenzoic acids are produced, the one melting at 251°, the other, much more soluble in water, at 141°. In both the nitro-group is contained in the ortho-position and hence in reduction both yield (1, 2) = (1, 6)-amidobenzoic acid (p. 562). The halogen of the nitro-haloid benzoic acids is very reactive (compare p. 588, *Berichte*, 22, 3282).

Dinitrobenzoic Acid, $C_6H_3(NO_2)_2.CO_2H$ (1, 2, 4—CO_2H in 1), is formed by oxidizing *α*-dinitro-toluene with fuming nitric acid, and consists of long prisms, melting at 169°. In the reduction with tin and hydrochloric acid the carboxyl group is split off and (1, 3)-diamidobenzene results.

The nitration of (1, 3)-nitrobenzoic acid with nitric and sulphuric acid produces the *symmetrical dinitrobenzoic acid* (1, 3, 5), which is also obtained by oxidizing symmetrical dinitrotoluene. It crystallizes from water in large quadratic plates, melting at 205°. Its reduction affords diamidobenzoic acid which yields (1, 3)-diamidobenzene, when distilled with baryta.

The nitration of (1, 2)-nitrobenzoic acid produces three *dinitrobenzoic acids:* (1, 2, 6), (1, 2, 5) and (1, 2, 4)—the latter being identical with the acid obtained from *α*-dinitrotoluene. The first acid melts at 202° and when heated decomposes into carbon dioxide and (1, 3)-dinitrobenzene. The second melts at 177° and when reduced yields a diamidobenzoic acid which affords (1, 3)-diamido-benzene when distilled with baryta (see the diamido-benzoic acids).

Amido-benzoic Acids, $C_6H_4(NH_2).CO_2H$.

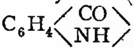
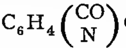
These are obtained by reducing the corresponding nitrobenzoic acids with tin and hydrochloric acid, or with hydrogen sulphide in ammoniacal solution. In the latter case the amido-acid is precipitated from the solution by acetic acid. They are also formed by the oxidation of the acetyl toluidines (p. 623). Dimethylated amido-acids are produced by the action of phosgene ($COCl_2$) upon the dimethylanilines (p. 739): or by methylating the acids by heating them with alkyl iodides and caustic alkali. Like glycocoll, the amido-benzoic acids yield crystalline salts both with acids and bases.

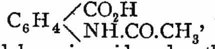
Ortho-amidobenzoic Acid (1, 2) also results from the two nitro-metabrombenzoic acids (p. 747) by reduction, and by the action of sodium amalgam. It was first obtained from *indigo*, hence termed *anthranilic acid.*

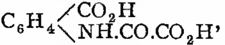
It is prepared by oxidizing indigo. This is effected by boiling it with manganese dioxide and sodium hydroxide (*Annalen*, 234, 146), or more readily if ortho-nitrobenzoic acid be reduced with tin and hydrochloric acid. Also by the oxidation of aceto-ortho-toluidine with potassium permanganate and boiling with hydrochloric acid.

The formation of dibromanthranilic acid, when bromine acts upon boiling orthonitrotoluene (p. 590), is worthy of note.

Anthranilic acid sublimes in long needles, is readily soluble in hot water and alcohol, melts at 144°, and decomposes into carbon dioxide and aniline when rapidly heated. Nitrous acid converts it, in aqueous solution, into salicylic acid.

The inner anhydride (lactam) of ortho-amidobenzoic acid is the so-called **Anthranil**,  $C_6H_4\langle{}^{CO}_{NH}\rangle$ (see *Berichte*, 20, 1537), obtained by the reduction of *o*-nitrobenzaldehyde with ferrous sulphate (theoretical quantity) and ammonia (*Berichte*, 15, 2572), or with tin and glacial acetic acid (*Berichte*, 15, 2105; 16, 2227). It also results when *o*-nitro-phenyloxyacrylic acid is boiled with water (*Berichte*, 16, 2222). It is an oil which volatilizes readily with aqueous vapor, possesses a peculiar odor and boils with decomposition about 210°. It dissolves in alkalies, forming salts of anthranilic acid. *o*-Amidobenzaldehyde and benzalcohol are produced when it is reduced. Chlorcarbonic esters produce **Anthranilcarbonic Acid**,  $C_6H_4\left({}^{CO}_{N}\right)CO_2H$, or  $C_6H_4\langle{}^{CO\text{———}}_{NH.CO}\rangle O$ (*Berichte*, 22, 1676), which may also be obtained by oxidizing a glacial acetic acid solution of isatin and indigo with chromic acid (hence called isatoic acid, *Berichte*, 17, Ref. 488). It crystallizes from hot water or alcohol in colorless needles or plates. It dissolves with much difficulty in most solvents. It melts about 233–240°, decomposing at the same time into carbon dioxide and anthranil. Digested with alkalies or boiled with acids, it decomposes into carbon dioxide and anthranilic acid. See *Berichte*, 19, Ref. 66 upon *p*-methylisatoic acid.

Acetyl-anthranilic Acid,  $C_6H_4\langle{}^{CO_2H}_{NH.CO.CH_3}$, results when acetyl-*o*-toluidine is oxidized, when *o*-amidobenzoic acid and anthranil (see above) are acted upon with acetic anhydride, and in the oxidation of methyl ketol and quinaldine (see these). It forms flat needles, melts at 180° and is readily decomposed into acetic and anthranilic acids. **Benzoyl-anthranilic Acid** melts at 182°.

o-**Benzam-oxalic Acid**,  $C_6H_4\langle{}^{CO_2H}_{NH.CO.CO_2H}$, Oxalyl-amido-benzoic acid, carbostyrilic acid, kynuric acid, is prepared synthetically by heating anthranilic acid with oxalic acid to 130° (*Berichte*, 17, 401 and Ref. 110); it is also obtained from indoxylic acid, from carbostyril, aceto-tetra-hydroquinoline, kynurene and kynurenic acid (see these). It crystallizes from hot water in long needles containing one molecule of water ($C_9H_7NO_5.H_2O$), and melts with decomposition at 200°. In a dessicator, more rapidly at 70–80°, it loses water and evolves carbon dioxide at 100°. When digested with alkalies it is decomposed into anthranilic and oxalic acids. Its *ethyl ester*, from the ester of indoxanthinic acid (*Berichte*, 15, 778), melts at 180°.

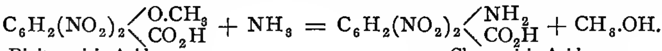
Similar compounds, *e. g.*, benzamoxalic acid, are prepared, too, from meta-amidobenzoic acid, by means of oxalic and malonic acids (*Berichte*, 18, 214; see also *Berichte*, 19, Ref. 252).

Meta-amidobenzoic Acid (1, 3), from *m*-nitrobenzoic acid, consists of aggregations of needles, dissolves readily in hot water and melts at 173–174°. It reacts acid, forming salts with acids and bases. The *ethyl ester*, obtained by reducing *m*-nitrobenzoic ester, is a thick oil. When in aqueous solution nitrous acid converts it into ordinary oxy-benzoic acid. Cyanogen chloride acts on it to form *m*-cyanamido-benzoic acid, $C_6H_4{<}\substack{CO_2H\\NH.CN}$. This yields uramido-benzoic acid, $C_6H_4{<}\substack{CO_2H\\NH.CO.NH_2}$, with hydrochloric acid (p. 392). The latter is also produced by fusing together meta-amido-benzoic acid and urea, or by mixing the hydrochloric acid salt with potassium cyanate. It contains one molecule of water, and forms small needles. When heated it becomes urea-dibenzoic acid, $CO(NH.C_6H_4.CO_2H)_2$ (*Berichte*, 15, 2122).

Para-amidobenzoic Acid, from para-nitrobenzoic acid, or from para-toluidine, crystallizes in needles, is rather easily soluble in water, and melts at 186–187°. Nitrous acid converts it into para-oxybenzoic acid.

The amido-benzoic acids, just like the anilines (p. 653), are changed, through the diazo-compounds, into **Hydrazine-benzoic Acids**, $C_6H_4{<}\substack{CO_2H\\NH.NH_2}$. Of these the ortho-body (from anthranilic acid), is the one which, when exposed to a temperature of 230°, forms the *inner anhydride*, $C_6H_4{<}\substack{CO\text{———}\\NH.NH}{>}$ (*Berichte*, 14, 478).

Dinitro-para-amidobenzoic Acid, $C_6H_2(NO_2)_2{<}\substack{NH_2\\CO_2H}$, **Chrysanisic Acid**, results when dinitro-anisic and dinitro-ethyl para-oxybenzoic acids are digested with aqueous ammonia. The group $O.CH_3$ is supplanted by NH_2 (p. 593):—



$$C_6H_2(NO_2)_2{<}\substack{O.CH_3\\CO_2H} + NH_3 = C_6H_2(NO_2)_2{<}\substack{NH_2\\CO_2H} + CH_3.OH.$$

Dinitroanisic Acid. Chrysanisic Acid.

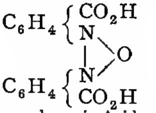
Chrysanisic acid forms light, golden-yellow leaflets or needles, melts at 259° and sublimes.

Diamidobenzoic Acids, $C_6H_3(NH_2)_2.CO_2H$. Four of the six possible isomerides are known. The elimination of CO_2 by one of them gives rise to para-phenylene diamine, two others yield ortho-, and the third meta-phenylene diamine. These acids conduct themselves towards the diazo-benzene-sulphonic acids, just the same as the corresponding phenylene-diamines (*Berichte*, 15, 2197).

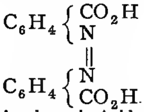
Triamido-benzoic Acid, $C_6H_2(NH_2)_3.CO_2H$ (1, 3, 4, 5—CO_2 in 1), has been obtained from dinitro-para-amidobenzoic acid. It yields (1, 2, 3)-triamido-benzene upon distillation (p. 625). For the isomeric acid (1, 3, 5, 6) see *Berichte*, 15, 2200.

AZO-BENZOIC ACIDS.

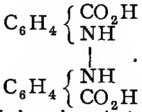
The action of sodium amalgam upon the mononitro-benzoic acids produces (same as from the nitrobenzenes) azoxy-, azo- and hydrazo-benzoic acids (p. 640):—



Azoxy-benzoic Acids.



Azo-benzoic Acids.



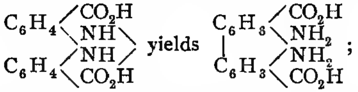
Hydrazo-benzoic Acids.

***m*-Azobenzoic Acid**, $C_{14}H_{10}N_2O_4 + \frac{1}{2}H_2O$, azo-benzene-*m*-dicarboxylic acid, is precipitated by hydrochloric acid as a yellow, amorphous powder, and dissolves with difficulty in water, alcohol and ether. When distilled it sustains decomposition. It is a dibasic acid, and yields crystalline yellow salts and ethers. Azobenzene is formed by the distillation of the copper salt; the calcium salt yields azodiphenylene, $C_{12}H_8N_2$. *Para-azo-benzoic acid* is a red, amorphous powder.

An *azobenzene-mono-carboxylic acid*, $C_6H_5.N_2.C_6H_4.CO_2H$, has been obtained from amido-azobenzene by replacing its amido-group by cyanogen, etc. (*Berichte*, 19, 3022).

m-**Azoxy-benzoic Acid**, $C_{14}H_{10}N_2O_5$ (1, 3), is formed when the alcoholic solution of meta-nitrobenzoic acid is boiled with potassium hydroxide. Hydrochloric acid precipitates it in yellowish masses.

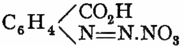
m-**Hydrazo-benzoic Acid**, $C_{14}H_{12}N_2O_4$ (1, 3), is obtained when ferrous sulphate is added to the boiling sodium hydroxide solution of *m*-azobenzoic acid. Hydrochloric acid precipitates the acid in yellow flakes from the filtered solution. It is not very soluble in hot alcohol. The aqueous solution of its salts absorbs oxygen, and changes to azobenzoic acid. When boiled with hydrochloric acid it is converted into the isomeric diamido-diphenyl-dicarboxylic acid (diamidodiphenic acid), derived from diphenyl:—



$$\begin{array}{l}C_6H_4\left\langle\begin{array}{l}CO_2H\\NH\end{array}\right.\\C_6H_4\left\langle\begin{array}{l}NH\\CO_2H\end{array}\right.\end{array}\text{ yields }\begin{array}{l}C_6H_3\left\langle\begin{array}{l}CO_2H\\NH_2\end{array}\right.\\\ |\\C_6H_3\left\langle\begin{array}{l}NH_2\\CO_2H\end{array}\right.\end{array};$$

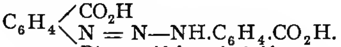
this resembles the formation of benzidine from hydrazo-benzene (p. 650). The latter acid is converted, by distillation with baryta, into benzidine and carbon dioxide. Two additional isomeric acids are produced by reducing *m*-azo- and azoxybenzoic acids with stannous chloride (*Berichte*, 23, 913).

Diazo-compounds. The aromatic amido-acids, analogous to the anilines, form diazo- and diazo-amido-compounds (p. 629):—



$$C_6H_4\left\langle\begin{array}{l}CO_2H\\N{=}N.NO_3\end{array}\right.$$

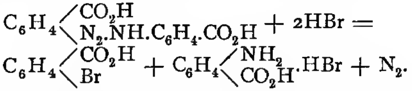
Diazo-benzoic Acid Nitrate.



$$C_6H_4\left\langle\begin{array}{l}CO_2H\\N=N\text{—}NH.C_6H_4.CO_2H.\end{array}\right.$$

Diazo-amidobenzoic Acid.

The diazo-compounds are produced by the action of nitrous acid upon salts of the amido-acids in aqueous or alcoholic solution, and sustain transpositions perfectly similar to those of other diazo-compounds. The addition of nitrous acid to the alcoholic solution of the free amido-acids causes the separation of the diazo-amido acids, which dissolve with difficulty. These are produced, too, on mixing solutions of the nitrates of the diazo-acids with amido-acids. When boiled with haloid acids they decompose into substituted acids and amido-acids, which continue dissolved as salts:—



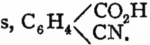
$$C_6H_4\left\langle\begin{array}{l}CO_2H\\N_2.NH.C_6H_4.CO_2H\end{array}\right. + 2HBr =$$
$$C_6H_4\left\langle\begin{array}{l}CO_2H\\Br\end{array}\right. + C_6H_4\left\langle\begin{array}{l}NH_2\\CO_2H\end{array}\right..HBr + N_2.$$

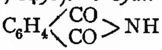
The sulphates of the diazobenzoic acids, when boiled with hydrochloric, hydrobromic and hydrofluoric acids, are similarly converted into their corresponding halogen benzoic acids. Hydriodic acid reacts at the ordinary temperatures (*Berichte*, 18, 960).

m-Diazobenzoic Acid Nitrate, $C_7H_5N_2O_2.NO_3$, from (1, 3)-amidobenzoic acid, is soluble with difficulty in cold water, and separates in colorless prisms which explode with violence. Caustic potash precipitates a yellow and very unstable mass from the aqueous solution. This is probably the free acid. Boiling water changes it to *m*-oxybenzoic acid. Bromine precipitates the *perbromide*, $C_7H_5N_2O_2Br_3$, as an oil, from the aqueous solutions; it solidifies in yellow prisms. It yields metabrombenzoic acid when digested with alcohol. Aqueous ammonia converts the perbromide into the *diazoimide*, $C_7H_5N_2O_2N$ (p. 640), which crystallizes from alcohol and ether in white leaflets. It is an acid, and forms salts with bases.

Diazo-m-amidobenzoic Acid, $C_{14}H_{11}N_3O_4$, is precipitated as an orange-red crystalline powder when nitrous acid is led into the alcoholic solution of meta-amidobenzoic acid. It is almost insoluble in water, alcohol and ether. It is a feeble, dibasic acid; its salts are very unstable in aqueous solution. When heated with the haloid acids it yields the corresponding halogen benzoic acids (see above).

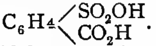
Ortho- and para-amido-benzoic acids yield corresponding diazo- and diazo-amido-compounds.

Cyanbenzoic Acids,  $C_6H_4\left<\begin{array}{l}CO_2H\\CN.\end{array}\right.$

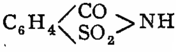
These are formed on boiling the HCl-diazo-benzoic acids with potassium cyanide and copper sulphate in aqueous solution (p. 633) (*Berichte*, 18, 1496). *o-Cyanbenzoic Acid* rearranges itself in its formation to phthalimide,  $C_6H_4\left<\begin{array}{l}CO\\CO\end{array}\right>NH$ (*Berichte*, 19, 2283).

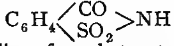
m-Cyanbenzoic Acid is readily soluble in ether, alcohol and hot water. It is a white microcrystalline powder, melting at 217°, and subliming with partial decomposition. It forms isophthalic acid on boiling with the alkalies (*Berichte*, 20, 524).

p-Cyanbenzoic Acid consists of microscopic needles, melting at 214°. It yields dicyanbenzophenone by the distillation of its calcium salt (*Berichte*, 20, 521).

Sulpho-benzoic Acids,  $C_6H_4\left<\begin{array}{l}SO_2OH\\CO_2H\end{array}\right.$.

On heating benzoic acid for some time with fuming sulphuric acid, or by conducting the vapors of SO_3 into the acid, we obtain as chief product *Metasulphobenzoic Acid*, and in smaller amount *Parasulphobenzoic Acid.*

The three isomerides can be obtained by oxidizing the three toluene sulphonic acids with an alkaline solution of potassium permanganate (p. 665). The *sulphamides* or sulphamin-benzoic acids,  $C_6H_4\left<\begin{array}{l}CO_2H\\SO_2NH_2\end{array}\right.$, are similarly obtained from the toluene sulphamines, $C_6H_4(CH_3).SO_2.NH_2$ (by potassium permanganate or potassium ferricyanide *Berichte*, 21, 242). The *ortho*-derivative eliminates water and passes readily into its inner anhydride—*benzoic-sulphinide*,  $C_6H_4\left<\begin{array}{l}CO\\SO_2\end{array}\right>NH$ (*Berichte*, 20, 1596; 22, 754, Ref. 662, 822).

o-Sulphobenzoic Acid dissolves readily in water, crystallizes in large tablets and melts at 250°. Its amide-anhydride—*benzoic-sulphinide*,  $C_6H_4\left<\begin{array}{l}CO\\SO_2\end{array}\right>NH$ (see above), dissolves in cold water with difficulty, and crystallizes from hot water or alcohol in delicate needles, melting at 224°. It possesses an exceedingly sweet taste (1 part = 200 parts cane sugar), hence has been called *Saccharin*. It has been employed as a substitute for sugar in the case of diabetic patients (Tech. Preparation, *Berichte*, 19, Ref. 375 and 471; 21, Ref. 100). When the sulphinide is evaporated to dryness with hydrochloric acid it changes to the ammonium salt of sulphobenzoic acid. Commercial saccharin contains 43–48 per cent. of sulphinide and 50 per cent. of para-sulphamine benzoic acid (*Berichte*, 22, Ref. 822). In aqueous solution the sulphinide has a somewhat acid character being able to form imide salts, $C_6H_4\left\langle\begin{matrix}CO\\SO_2\end{matrix}\right\rangle NMe$, which are different from the salts of sulphamin-benzoic acid, $C_6H_4\left\langle\begin{matrix}CO_2Me\\SO_2NH_2\end{matrix}\right.$.

The alkyl iodides convert the sulphinide salts into ethers (*Berichte*, **21**, Ref. 100). For the methyl saccharin from *p*-toluidine sulphonic acid, consult *Berichte*, **22**, Ref. 719).

HOMOLOGUES OF BENZOIC ACID.

Acids, $C_8H_8O_2$.

1. Toluic Acids, $C_6H_4\left\langle\begin{matrix}CH_3\\CO_2H\end{matrix}\right.$, Methyl-benzoic Acids.

The three toluic acids are produced when the three xylenes are boiled for some time with dilute nitric acid (p. 571), and also by the action of sodium and carbon dioxide, or chlorcarbonic esters, upon brom- and iodo-toluene. The easiest course to pursue consists in converting the three toluidines into tolunitriles, then saponifying the latter with the alkalies or sulphuric acid (of 75 per cent.) (see *Berichte*, **19**, 756).

Orthotoluic Acid (1, 2) results upon heating phthalide with phosphorus and hydriodic acid (*Berichte*, **20**, Ref. 378). It crystallizes from hot water in long needles, melting at 102.5°. It is very volatile with steam. The *calcium salt*, $(C_8H_7O_2)_2Ca + 2H_2O$, and the *barium salt*, $(C_8H_7O_2)_2Ba + 2H_2O$, are readily soluble in water, and crystallize in delicate needles. Chromic acid decomposes it, yielding carbon dioxide; potassium permanganate forms phthalic acid.

Metatoluic Acid (1, 3) is obtained by oxidizing pure xylene with dilute nitric acid (p. 573) (pure metaxylene is only oxidized at 130–150°). The most satisfactory course for its preparation consists in oxidizing *m*-xylene sulphamide with potassium permanganate, and then decomposing the sulphamide that results with hydrochloric acid (*Berichte*, **14**, 2349). It is more soluble in water than its two isomerides, and crystallizes in minute needles, melting at 110° and boiling at 263°. It is easily volatilized with aqueous vapor. Chromic acid oxidizes it with ease to isophthalic acid. Its *calcium salt*, $(C_8H_7O_2)_2Ca + 3H_2O$, is very soluble in water.

Paratoluic Acid (1, 4) is obtained by boiling paraxylene or cymene for several days with dilute nitric acid. It crystallizes from alcohol or hot water in needles, melting at 180°; it boils at 275° (corrected). It is very volatile with steam. Nitric acid or chromic acid oxidizes it to terephthalic acid.

2. **Phenyl-acetic Acid**, $C_6H_5.CH_2.CO_2H$, **Alphatoluic Acid**, is obtained: from benzyl cyanide, $C_6H_5.CH_2.CN$, when boiled with alkalies; from mandelic acid, $C_6H_5.CH(OH).CO_2H$, by heating with hydriodic acid; from vulpic acid by boiling with baryta; and from brombenzene and monochloracetic ester by means of sodium.

To prepare it benzaldehyde is first changed to phenyl-chloracetic acid, $C_6H_5.CHCl.CO_2H$ (see mandelic acid) and the latter then reduced by zinc dust, in ammoniacal solution (*Berichte*, **14**, 240). A better procedure consists in boiling benzyl chloride with potassium cyanide, then saponifying the latter with caustic potash, or with moderately dilute sulphuric acid (*Berichte*, 19, 1950), which is a simpler method. The ethyl ester can be directly obtained from the cyanide by conducting hydrochloric acid gas into its alcoholic solution (*Berichte*, 20, 592).

Phenyl-acetic acid crystallizes in shining leaflets, resembling those of benzoic acid; it melts at 76.5°, and boils without decomposition at 262°. Benzoic acid is formed when it is oxidized with chromic acid. The *methyl ester*, $C_8H_7O_2.CH_3$, boils at 220°; the *ethyl ester* at 226°.

The CH_2-group of phenylacetic esters, $C_6H_5.CH_2.CO_2R$, cannot be replaced by alkyls (distinction from benzyl cyanide, p. 734) (*Berichte*, 21, 1306).

Phosphorus pentachloride converts the acid into phenyl acetic chloride, $C_6H_5.CH_2.COCl$, which boils at 102° under a pressure of 17 mm. It forms desoxybenzoin with benzene and aluminium chloride (*Berichte*, 20, 1389). *Phenylacetic anhydride*, $(C_6H_5.CH_2CO)_2O$, is produced by the action of the chloride upon silver phenylacetate. It melts at 72°.

If the acid be acted upon by chlorine or bromine in the cold the halogens will enter the benzene nucleus and in the para-position; if heat be applied the side-chain will be substituted. The latter mono-halogen derivatives are also produced from mandelic acid, $C_6H_5.CH(OH).CO_2H$, if it be heated with hydrochloric or hydrobromic acid to 130–140°, and when boiled with alkalies regenerate mandelic acid. **Phenyl-chloracetic Acid**, $C_6H_5.CHCl.CO_2H$, is also directly prepared from CNH-benzaldehyde (see Mandelic Acid), crystallizes in leaflets, and melts at 78°. **Phenyl-bromacetic Acid** melts at 83–84°, and when potassium cyanide acts upon its ester diphenyl-succinic acid is produced.

Phenyl-isonitroso-acetic Acid, $C_6H_6.C(N.OH).CO_2H$, is produced from phenyl-glyoxylic acid (p. 762) with hydroxylamine and from isonitrosobenzyl cyanide, $C_6H_5.C(N.OH).CN$; it melts at 128°. The *ethyl ester*, melting at 113°, has been obtained from nitrophenyl-isonitroso acetic ester (*Berichte*, 16, 519).

Phenyl-amido-acetic Acid, $C_6H_5.CH(NH_2).CO_2H$, results from phenyl-isonitroso-acetic acid by reduction with tin and hydrochloric acid; from phenyl-bromacetic acid with ammonia, and from CNH-benzaldehyde, $C_6H_5.CH(OH).CN$, by ammonia and saponification. It consists of pearly leaflets, melting at 256°. It decomposes, when distilled, into carbon dioxide and benzylamine.

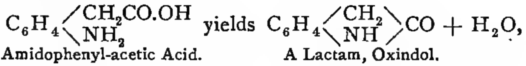
Nitrophenyl-acetic Acids, $C_6H_4(NO_2).CH_2.CO_2H$.

The para-nitro acid, with a small amount of the ortho-nitro acid, is produced on dissolving phenyl-acetic acid in cold, fuming nitric acid. These acids can be separated by means of their barium salts. The three nitro-acids may be obtained synthetically from the three nitrobenzyl cyanides, $C_6H_4(NO_2).CH_2.CN$ (p. 735).

o-**Nitrophenyl-acetic Acid** crystallizes from hot water in needles, melts at 141° (137°), and by oxidation yields *o*-nitrobenzoic acid. *m*-**Nitrophenyl-acetic Acid** melts at 120°. *p*-**Nitrophenyl-acetic Acid** dissolves with difficulty in water, and melts at 152°. Further nitration of ortho- and para-nitrophenyl-acetic acid produces *op*-**Dinitrophenyl-acetic Acid** (1, 2, 4), melting at 160°, and decomposing into carbon dioxide and *op*-dinitro-toluene. Its *methyl ester* melts at 82°, and the *ethyl ester* at 35°. These dissolve in alcoholic alkalies, forming deep-red colored salts, *e. g.*, $C_6H_3(NO_2)_2.CHNa.CO_2R$, the metal of which can be replaced by other radicals (*Berichte*, 21, 1307, 2475). Diazobenzene chloride produces an azo- or hydrazone derivative. Its potassium salt, $C_6H_3(NO_2)_2.C(N.NNa.C_6H_5).CO_2R$, is deep blue in color, and is capable of entering a remarkable transposition, leading to the formation of a pyrazole derivative (*Berichte*, **22**, 320; **23**, 1574).

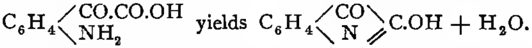
Amidophenyl-acetic Acids, $C_6H_4(NH_2).CH_2.CO_2H$.

These can be obtained by reducing the nitro-acids. The ortho-compound and other ortho-amido-acids can, by the exit of water, form amide-anhydrides. This is analogous to the formation of lactones (p. 351) from oxy-acids. The oxygen may be taken from the hydroxyl or from the CO-group of carboxyl; in the first instance so-called *lactams* (inner amides) are produced, in the latter the *lactimes* (inner imides):—



$$C_6H_4\left\langle\begin{array}{l}CH_2CO.OH\\NH_2\end{array}\right. \text{ yields } C_6H_4\left\langle\begin{array}{c}CH_2\\NH\end{array}\right\rangle CO + H_2O,$$

o-Amidophenyl-acetic Acid. A Lactam, Oxindol.

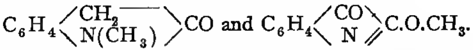


$$C_6H_4\left\langle\begin{array}{l}CO.CO.OH\\NH_2\end{array}\right. \text{ yields } C_6H_4\left\langle\begin{array}{c}CO\\N\end{array}\right\rangle C.OH + H_2O.$$

o-Amidophenyl-glyoxylic Acid. A Lactime, Isatin.

This anhydride formation sometimes occurs spontaneously in the separation of the free acids from their salts (or in the reduction of the nitro-compounds).

As yet, *but one* anhydride (lactam or lactime) has been obtained from each acid; the other form cannot necessarily be designated the unstable or pseudo form; however, the two forms may probably be tautomeric (p. 54). These anhydrides do yield two entirely different series of alkyl derivatives, depending upon whether the hydrogen of the NH-group in the *lactam ethers*, or the H of hydroxyl in the *lactime ethers*, is replaced by alkyl, *e.g.*:—

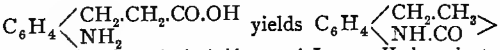


$$C_6H_4\left\langle\begin{array}{c}CH_2\\N(CH_3)\end{array}\right\rangle CO \text{ and } C_6H_4\left\langle\begin{array}{c}CO\\N\end{array}\right\rangle C.O.CH_3.$$

Lactam Ether, Methyl Oxindol. Lactime Ether, Methyl Isatin.

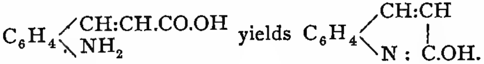
The ethers of the lactams (in which the alkyl is attached to nitrogen) are very stable, whereas the lactimes are decomposed by heating with hydrochloric acid. It is possible to prepare both varieties of ethers with many of the anhydrides. This would indicate that the two anhydride forms are identical (see Carbostyril and *Berichte*, **18**, 1528; **20**, 2009).

The acids, with 2 and 3 carbon atoms in the side-chain, condense in this way; the former yield indol-, the latter quinoline-derivatives:—



$$C_6H_4\left\langle\begin{array}{l}CH_2.CH_2.CO.OH\\NH_2\end{array}\right. \text{ yields } C_6H_4\left\langle\begin{array}{l}CH_2.CH_2\\NH.CO\end{array}\right\rangle$$

o-Amidophenyl-propionic Acid. A Lactam, Hydrocarbostyril.



$$C_6H_4\left\langle\begin{array}{l}CH{:}CH.CO.OH\\NH_2\end{array}\right. \text{ yields } C_6H_4\left\langle\begin{array}{l}CH{:}CH\\ \qquad\ \ |\\N : C.OH.\end{array}\right.$$

o-Amidophenyl-acrylic Acid. A Lactime, Carbostyril.

The indol-bodies contain a chain of 4 C-atoms (2 of which belong to the benzene nucleus), closed by 1 N-atom (a chain of 5 members)—analogous to the pyrrol compounds (p. 538); they may also be compared to the γ-lactones and the furfurane compounds. In the quinoline derivatives we have a chain of 5 C-atoms, the same as in the δ-lactones. A ring of 3 C-atoms linked by N has only been confirmed in the case of anthranil (p. 749); it is, however, analogously very unstable, as in the β-lactones (p. 353).

The ortho-amido-derivatives of the aldehydes and ketones, in which the CO-group represents the second or third member of the side-chain, are capable, too, of condensing and producing compounds belonging to the indol- and quinoline-groups. Thus, from *o*-amidophenyl-acetaldehyde we get indol (p. 721); from *o*-amidophenyl-acetone, methyl ketol (p. 730); and from *o*-amidobenzyl-acetone, hydromethyl-quinoline (p. 730). Yet, chains (with 6 and more C-atoms and 1 N-atom) having 7 or more members, could not be produced (*Berichte*, 13, 122; 14, 481; 20, 377).

***o*-Amidophenyl-acetic Acid** passes immediately into its lactam, oxindol, when it is produced (by reduction of the ortho-nitro-acid). When oxindol is heated to 150° with baryta water, water is absorbed and the barium amidophenyl-acetate produced. Acids liberate oxindol from it (*Berichte*, 16, 1704).

Acetyl-o-amido phenyl-acetic Acid, $C_6H_4(NH.CO.CH_3).CH_2.CO_2H$, is obtained by dissolving acetyl oxindol in dilute sodium hydroxide; it melts at 142°, and when heated with alkalies or acids decomposes into oxindol and acetic acid.

***m*-Amidophenyl Acetic Acid**, from the nitro-acid, crystallizes from hot water in leaflets, and melts at 149°. ***p*-Amidophenyl-acetic Acid**, from the nitro-acid, consists of pearly leaflets, and melts at 200°.

When dinitrophenyl-acetic acid (p. 754) is reduced with tin and hydrochloric acid, **Diamido-phenyl-acetic Acid** results, and this immediately passes into *p*-amido-oxindol, $C_6H_6(NH_2)NO$. Partial reduction of the dinitro-acid with ammonium sulphide yields *p*-amido-*o*-nitro-phenyl-acetic acid, $C_6H_3(NH_2)(NO_2).CH_2.CO_2H$. This treated with amyl nitrite and alcohol yields ***o*-Nitrophenyl-isonitroso-acetic Acid**, $C_6H_4(NO_2).C(N.OH).CO_2H$, and *o*-nitrobenzaldoxime (p. 720). Isomeric ***p*-Amido-*m*-nitrophenyl-acetic Acid**, from *p*-amidophenyl acetic acid, yields *m*-nitrobenzaldoxime with the same reagents. An isomeric **Pseudophenyl-acetic Acid**, $C_8H_8O_2$, seems to have been prepared by the action of diazo-acetic ester upon benzene (p. 207). Homologous acids have been formed in the same way (*Berichte*, 18, 2377).

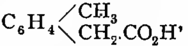
Acids, $C_9H_{10}O_2$.

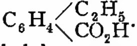
1. Dimethylbenzoic Acids, $C_6H_3(CH_3)_2.CO_2H$. Four of the six possible acids with this formula are known.

Mesitylenic Acid has the symmetrical structure (1, 3, 5), and is obtained by gradually oxidizing mesitylene with dilute nitric acid. It crystallizes from alcohol in large prisms, from water in needles; it melts at 166° and sublimes very readily. The *barium salt*, $(C_9H_9O_2)_2Ba$, is very soluble in water and consists of large, shining prisms. The *ethyl ester*, $C_9H_9(C_2H_5)O_2$, solidifies at 0° and boils at 241°. Distilled with excess of lime, mesitylenic acid yields isoxylene. Nitric acid oxidizes it further to uvitic and trimesic acids.

The oxidation of pseudocumene (p. 574) with dilute nitric acid produces xylic acid, $C_6H_3(CH_3)_2.CO_2H$(1, 2, 4—CO_2H in 1), and so called **para-xylic acid** (1, 3, 4); both distil with aqueous vapor and can be separated by means of their calcium salts. Xylic acid has also been obtained from bromisoxylene by the action of sodium and carbon dioxide. From alcohol it crystallizes in long prisms, dissolves with difficulty in water, melts at 126° and sublimes readily. Its *calcium salt*, $(C_9H_9O_2)_2Ca + 2H_2O$, forms thick prisms and is more easily soluble in water than the salt of paraxylic acid. Isoxylene results when it is distilled with lime. Nitric acid oxidizes it to xylidic acid, $C_6H_3(CH_3).(CO_2H)_2$; chromic acid decomposes it into carbon dioxide.

Paraxylic acid crystallizes from alcohol in concentrically grouped needles and melts at 163°. Its *calcium salt* contains three and one-half molecules of water and consists of needles. Distilled with lime it yields ortho-xylene; both methyl groups, therefore, occur in the ortho-place. Oxidation converts it into xylidic acid.

2. **Tolyl-acetic Acids,**  $C_6H_4\begin{matrix}/CH_3\\ \backslash CH_2.CO_2H\end{matrix}$, **Alpha-xylic Acids.** The three isomeric acids have been obtained from the three xylene bromides, $C_6H_4(CH_3).CH_2.Br$, by means of the cyanides (*Berichte*, 15, 1744). The *ortho*-acid melts at 89°; the *meta* at 61°, and the *para* at 91°. The latter acid has also been obtained from tolylglyoxylic acid by reduction with hydriodic acid and phosphorus. It melts at 72° (*Berichte*, 20, 2051).

3. *Ethyl-benzoic Acids,*  $C_6H_4\begin{matrix}/C_2H_5\\ \backslash CO_2H\end{matrix}$. The para-acid (1, 4) may be obtained by oxidizing para-diethyl benzene with nitric acid, and from para-bromethyl benzene, $C_6H_4Br.C_2H_5$, by the action of sodium and carbon dioxide. It crystallizes in leaflets from hot water, melts at 112° and sublimes readily. Oxidation converts it into terephthalic acid. The *ortho-acid* is formed by reducing acetophenone carbonic acid with hydriodic acid. It melts at 62°.

(4) The *phenylpropionic acids*, $C_6H_5.C_2H_4.CO_2H$, are hydrocinnamic acid and hydroatropic acid:—

(*a*) **Hydrocinnamic Acid,** $C_6H_5.CH_2.CH_2.CO_2H$, **β-Phenyl-propionic Acid,** is obtained: by the action of sodium amalgam upon cinnamic acid (phenylacrylic acid), or upon heating the latter with hydriodic acid (*Berichte*, 13, 1680); when potassium cyanide acts upon α-chlorethylbenzene, $C_6H_5.CH_2.CH_2Cl$ (p. 586); from benzyl aceto-acetic ester and benzyl malonic ester, also from benzylic acetic ester (p. 740); and in the decay of albuminoid substances. It is very soluble in hot water and alcohol, crystallizes in needles, melts at 47° and distils without decomposition at 280°. Chromic acid oxidizes it to benzoic acid.

Haloid Hydrocinnamic Acids, of the formula $C_6H_5.CHX.CH_2.CO_2H$, are obtained from cinnamic acid, $C_6H_5.CH{:}CH.CO_2H$, by the addition of the haloid acids (p. 223) and by the action of these upon β-phenyl-hydracrylic acid, $C_6H_5.CH(OH).CH_2.CO_2H$. On heating or boiling with water the free acids decompose (as β-oxyacids are produced at first, p. 346) into the haloid acid and cinnamic acid; when neutralized with alkaline carbonates they split up, even in the cold, into a halogen acid, carbon dioxide and styrolene, $C_6H_5.CH{:}CH_2$. **β-Chlor-hydro-cinnamic acid,** $C_6H_5.CHCl.CH_2.CO_2H$, melts at 126°; the brom-acid at 137°, the iodo-acid at 120°.

αβ-Dibromhydrocinnamic Acid, $C_6H_5.CHBr.CHBr.CO_2H$, **Cinnamic Bromide,** is formed by the addition of bromine to cinnamic acid (dissolved in

CS_2) (*Annalen*, 195, 140). It crystallizes from alcohol in leaflets, melts at 201°, and decomposes. When digested with a soda solution it is decomposed into α-bromstyrolene, $C_6H_5.CH:CBrH$, carbon dioxide and hydrobromic acid; when boiled with water phenyl α-brom-lactic acid is also produced. **$\alpha\beta$-Dichlorhydrocinnamic Acid** deports itself similarly, and melts at 163° (*Berichte*, 14, 1867).

α- and β-Monobrom-cinnamic acids are produced when dibromhydro-cinnamic acid is treated with alcoholic potassium hydroxide (see this).

Phenylamido-propionic Acids.

Phenyl-α-amido-propionic Acid, $C_6H_5.CH_2.CH(NH_2).CO_2H$, Phenylalanine, is produced from phenyl-acetaldehyde with prussic acid and ammonia (*Annalen*, 219, 186). It is soluble with difficulty in both cold water and hot alcohol. It crystallizes in leaflets or prisms. It does not part with ammonia when boiled with caustic potash or concentrated hydrochloric acid. It readily combines to form salts with bases and acids. When slowly heated it sublimes without decomposition; quickly heated phenyl ethylamine and a lactimide are produced. It also occurs in the sprouts (along with asparagine) of *Lupinus luteus*, and is formed in the decay of albumen (*Berichte*, 16, 1711).

The nitration of phenyl-alanine yields the *para-nitro*-compound, which by reduction becomes *p*-**Amidophenyl-alanine**, $C_6H_4(NH_2).CH_2.CH(NH_2).CO_2H$. The latter is also obtained in the reduction of dinitro-cinnamic acid, $C_6H_4(NO_2).CH:C(NO_2).CO_2H$ (*Berichte*, 16, 852), and when acted upon by one equivalent of nitrous acid forms tyrosine (*Annalen*, 219, 170).

Phenyl-β-amidopropionic Acid, $C_6H_5.CH(NH_2).CH_2.CO_2H$, is obtained on treating β-bromhydro-cinnamic acid with aqueous ammonia; it is easily soluble in water and alcohol, melts at 121°, and when boiled with acids decomposes into NH_3 and cinnamic acid. It does not combine with bases, and with difficulty with acids (*Berichte*, 17, 1498).

The **Halogen-hydrocinnamic Acids**, $C_6H_4.X.CH_2.CH_2.CO_2H$, containing the substitutions in the benzene nucleus, are obtained from the corresponding halogen cinnamic acids on heating them with hydriodic acid and phosphorus (*Berichte*, 15, 2301; 16, 2040).

Nitrohydrocinnamic Acids, $C_6H_4(NO_2).CH_2.CH_2.CO_2H$.

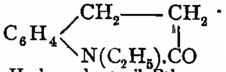
The nitration of hydrocinnamic acid produces the *para* and *ortho* acids, which can be separated by crystallization from water. *o*-**Nitrohydrocinnamic Acid** is more easily obtained from the dinitrohydrocinnamic acid (see below). It forms small yellow crystals, and melts at 113°.

m-**Nitrohydrocinnamic Acid** results from *p*-amido-*m*-nitrohydrocinnamic acid (see below) by the elimination of the amido-group, and melts at 118°. *p*-**Nitrohydrocinnamic Acid** melts at 163°, and is oxidized to *p*-nitrobenzoic acid by a chromic acid mixture.

Amido-hydrocinnamic Acids, $C_6H_4(NH_2).CH_2.CH_2.CO_2H$.

o-**Amido-hydrocinnamic Acid.** When this acid is formed by the reduction of *o*-nitrocinnamic acid with tin and hydrochloric acid it at once changes to its lactam, **Hydrocarbostyril**, C_9H_9NO (p. 755). The latter is intimately related to quinoline, C_9H_7N, dissolves readily in alcohol and ether, crystallizes in prisms melts at 160°, and distils undecomposed.

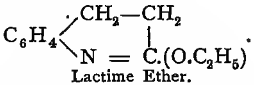
While the lactime of *o*-amido-hydrocinnamic acid is unstable, its ethers exist, as do those of the lactam (hydrocarbostyril) (p. 755):—



$$C_6H_4\left<\begin{matrix}CH_2 - CH_2 \\ N(C_2H_5).CO\end{matrix}\right.$$

Hydrocarbostyril Ether.

and



$$C_6H_4\left<\begin{matrix}CH_2 - CH_2 \\ N = C.(O.C_2H_5)\end{matrix}\right. .$$

Lactime Ether.

The former is produced from hydrocarbostyril by means of ethyl iodide and alcoholic potassium hydroxide; it is very stable; the latter, formed in the reduction of *o*-nitrohydrocinnamic ether, is saponified on heating with hydrochloric acid (*Berichte*, 15, 2103).

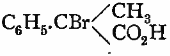
m-**Amidohydrocinnamic Acid**, prepared by reducing the *m*-nitro-acid with tin and hydrochloric acid, melts at 85°. *p*-**Amido-hydrocinnamic Acid** melts at 131°. Energetic nitration of hydrocinnamic acid produces *po*-dinitro-hydrocinnamic acid, $C_6H_3(NO_2)_2.C_2H_4.CO_2H$ (1, 2, 4), which melts at 126°. Reduction with ammonium sulphide affords *p*-**amido**-*o*-**nitrocinnamic acid**, melting at 139°. By the elimination of the NH_2-group we get *o*-nitrohydrocinnamic acid. The reduction of the dinitro-acid with tin and hydrochloric acid brings about condensation of the diamido-acid at once to *p*-**amido-hydrocarbostyril**, $C_9H_8(NH_2).NO$ (p. 756), melting at 211° (*Berichte*, 15, 842, 2291).

The *p*-**Amido**-*m*-**nitrohydrocinnamic Acid**, $C_6H_3(NH_2)(NO_2).C_2H_4.CO_2H$, is formed in the nitration of aceto-*p*-amidohydrocinnamic acid, melts at 145°, and by the elimination of the amido-group yields *m*-nitrohydrocinnamic acid.

(*b*) **Hydro-atropic Acid**, $C_6H_5.CH\left<\begin{matrix}CH_3 \\ CO_2H\end{matrix}\right.$, *a*-**Phenyl-propionic Acid**, is obtained from atropic acid, $C_9H_8O_2 = C_6H_5.C(CH_2).CO_2H$, by the action of sodium amalgam, and from acetophenone, $C_6H_5.CO.CH_3$, when acted upon with hydrocyanic and hydriodic acids (*Annalen*, 250, 135). It is an oil, boiling at 265°, and is volatile in aqueous vapor. Potassium permanganate oxidizes it to atrolactinic acid (p. 775) by changing tertiary hydrogen to hydroxyl.

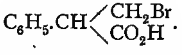
Bromhydro-atropic Acids:—

(*a*)



$$C_6H_5.CBr\left<\begin{matrix}CH_3 \\ CO_2H\end{matrix}\right.$$

(*β*)



$$C_6H_5.CH\left<\begin{matrix}CH_2Br \\ CO_2H\end{matrix}\right. .$$

Both isomerides result from the addition of HBr to atropic acid, $C_9H_8O_2$. The *a*-acid, obtained from atrolactinic acid, $C_9H_{10}O_3$, by means of hydrobromic acid, melts at 93°, and reverts to atrolactinic acid on boiling with a soda solution. The *β*-acid also melts at 93°, and when boiled with alkaline carbonates yields tropic acid, $C_9H_{10}O_3$, together with atropic acid and styrolene. The chlorhydro-atropic acids deport themselves similarly (*Annalen*, 209, 21).

p- and *o*-*Nitrohydro-atropic Acids* are obtained by nitrating hydro-atropic acid in the cold. The *para* acid melts at 88°, and by reduction yields *p*-amido-hydro-atropic acid, which by diazotizing passes into the *p*-oxy-acid (phloretinic acid). The ortho-nitro-acid yields an amido acid which immediately, by loss of water, passes into its lactam, atroxindol, $C_6H_4\left<\begin{matrix}CH(CH_3) \\ NH\end{matrix}\right>CO$ (p. 755) (*Berichte*, 18, Ref. 230).

Acids, $C_{10}H_{12}O_2$.

(1) Durylic Acid, $C_6H_2(CH_3)_3.CO_2H$, obtained by the oxidation of durene, crystallizes in hard prisms, and melts at 115°. The two hydrogen atoms in it occupy the para position; therefore, when diamido-durylic acid is oxidized its quinone, trimethylquinone carboxylic acid, is produced (*Berichte*, 18, 3496).

(2) The oxidation of isodurene affords three **Isodurylic Acids**, the α- melting at 215°, the β- at 151°, and γ- at 84°. When these split off carbon dioxide the corresponding trimethyl benzenes result; from the α we get hemi-mellithene, from the β, mesitylene and from the γ, pseudocumene (*Berichte*, 15, 1855).

(3) Propyl Benzoic Acids: six isomerides.

Cumic Acid,  $C_6H_4\begin{cases}C_3H_7\\CO_2H\end{cases}$, *p*-isopropyl benzoic acid (containing the isopropyl group), is produced by the oxidation of cuminic alcohol and aldehyde with dilute nitric acid, or by the action of potassium hydroxide (p. 709). It has been synthetically prepared from *p*-bromcumene, $C_6H_4Br.C_3H_7$ (with isopropyl, p. 575), by the action of sodium and carbon dioxide (*Berichte*, 15, 1903). It is furthermore produced by the oxidation of cymene (p. 577) in the animal organism; a transposition of normal propyl occurs in this case.

It is obtained from cuminol (Roman caraway oil) by fusion with caustic potash, or what is better, by the oxidation with an alkaline potassium permanganate solution (*Berichte*, 11, 1790).

Cumic acid is very soluble in water and alcohol, crystallizes in needles or leaflets, melts at 116°, and boils about 290°. It yields cumene (isopropyl benzene) when distilled with lime. Chromic acid oxidizes it to terephthalic acid and potassium permanganate converts it into oxypropyl-benzoic acid, $C_6H_4(C_3H_6.OH).CO_2H$, and acetobenzoic acid (p. 760).

Normal Cumic Acid, $C_6H_4(C_3H_7).CO_2H$, *p*-normal propylbenzoic acid (with normal propyl), is obtained by oxidizing propylisopropyl benzene and dinormal propyl benzene with dilute nitric acid (*Berichte*, 16, 417); also synthetically from *p*-brompropyl benzene, $C_6H_4Br.C_3H_7$ (with normal propyl), by the action of CO_2 and Na. It is volatile with aqueous vapor, crystallizes in shining needles or leaflets, and melts at 140°. *o-Normal Propyl-benzoic Acid* (1, 2), is produced when phthalyl propionic acid is reduced with hydriodic acid. It melts at 58°.

(4) **Tetramethylbenzene Carboxylic Acid,** $C_6H(CH_3)_4.CO_2H$, Durene Carboxylic Acid, results upon treating durene with phosgene in the presence of aluminium chloride. It melts at 179°, volatilizes with steam, and if heated to 200°, together with concentrated hydrochloric acid, breaks down into carbon dioxide and durene. Its *cyanide* is formed upon distilling the acid with lead sulphocyanide. It melts at 77° (*Berichte*, 22, 1223).

Pentamethyl Benzoic Acid, $C_6(CH_3)_5.CO_2H$, is formed from pentamethylbenzene by the action of phosgene and $AlCl_3$. It melts at 210°. If heated with lime or hydrochloric acid it breaks down into pentamethyl benzene and carbon dioxide. Its *cyanide*, $C_6(CH_3)_5.CN$, is produced in the same manner as that of the preceding acid. It cannot be saponified by acid or alkalies, but decomposes into ammonia, carbon dioxide and pentamethyl benzene (*Berichte*, 22, 1221).

Aldehyde Acids.

Phenyl Formyl Acetic Acid, $C_6H_5.CH(CHO).CO_2H$, belongs to this class. Its esters are obtained similarly to the ketonic esters (see below) by the action of sodium ethylate upon phenyl acetic esters, $C_6H_5.CH_2.CO_2R$, and formic esters, CHO.OR. It is an oily liquid, boiling at 144–145° under a pressure of 16 mm. Ferric chloride imparts a blue-violet coloration to its alcoholic solution. The free acid is very unstable. The ester, acting as a β-keton-compound, condenses with phenylhydrazine to diphenylpyrazolon (*Berichte*, 20, 2933).

KE

KETONIC ACIDS.

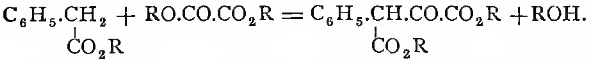
The acids of this class in the benzene series are perfectly analogous to those of the paraffin series. A rather remarkable method for their formation is that of the union of benzoic esters with fatty acid esters, alcohol being eliminated, and also the union of acetophenone, $C_6H_5.CO.CH_3$, with carbonic acid esters and esters of oxalic acid. The reaction is similar to that occurring in the formation of ketones (p. 726). It follows by the action of dry or alcoholic sodium ethylate upon a mixture of the two components (Claisen, *Berichte*, 20, 655, 2178), or by the action of metallic sodium (Wislicenus and Piutti, *Berichte*, 20, 589, 537, 2930):—

$$C_6H_5.CO.OR + \underset{\substack{\text{Acetic Acid}\\ \text{Ester.}}}{CH_3.CO_2R} = \underset{\substack{\text{Ester of Benzoyl}\\ \text{Acetic Acid.}}}{C_6H_5.CO.CH_2.CO_2R} + ROH,$$

$$C_6H_5.CO.CH_3 + \underset{\substack{\text{Carbonic Acid}\\ \text{Ester.}}}{RO.CO_2R} = C_6H_5.CO.CH_2.CO_2R + ROH,$$

$$C_6H_5.CO.CH_3 + RO.CO.CO_2R = \underset{\substack{\text{Benzoyl Pyroracemic}\\ \text{Acid.}}}{C_6H_5.CO.CH_2.CO.CO_2R} + ROH.$$

Phenyloxalacetic ester (*Berichte*, 20, 592) is similarly obtained from phenylacetic ester and oxalic ester:—



$$\underset{\substack{|\\ CO_2R}}{C_6H_5.CH_2} + RO.CO.CO_2R = \underset{\substack{|\\ CO_2R}}{C_6H_5.CH}.CO.CO_2R + ROH.$$

Phenyl pyroracemic acid, $C_6H_5.CH_2.CO.CO_2H$, is again obtained from this by the ketone decomposition (upon boiling with dilute sulphuric acid).

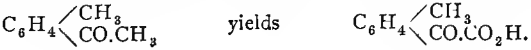
Nascent hydrogen converts all the ketonic acids into oxyacids.

1. α-Ketonic Acids.

These like those of the fatty series are produced (1) by the action of hydrochloric acid upon the cyanides of the acid radicals; (2) by the action of chloroxalic esters upon the benzenes in the presence of $AlCl_3$ (*Berichte*, 20, 2048):—

$$C_6H_6 + Cl.CO.CO_2.C_5H_{11} = C_6H_5.CO.CO_2.C_5H_{11} + HCl;$$

(3) by the oxidation of acetyl benzenes (containing a methyl group in addition to the acetyl group) with potassium permanganate or potassium ferricyanide (*Berichte*, 20, 2213; 23, Ref. 641):—



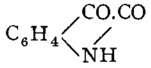
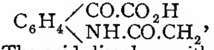
$$C_6H_4\begin{cases}CH_3\\ CO.CH_3\end{cases} \quad \text{yields} \quad C_6H_4\begin{cases}CH_3\\ CO.CO_2H.\end{cases}$$

1. **Benzoyl Formic Acid**, $C_6H_5.CO.CO_2H$, Phenylglyoxylic Acid, is obtained in the action of fuming hydrochloric acid at ordinary temperatures upon benzoyl cyanide, $C_6H_5.CO.CN$, and by oxidizing acetophenone with potassium ferricyanide (*Berichte*, 20, 389), as well as by oxidizing benzoyl carbinol, styrolene alcohol (p. 712) and mandelic acid with dilute nitric acid or permanganate. Its ethyl ester is formed when ethyl chloroxalic ester acts upon mercury diphenyl, or benzene in the presence of $AlCl_3$. The acid is separated from its salts in the form of an oil, which slowly solidifies on standing over sulphuric acid. It is very soluble in water, melts at 65–66°, and when distilled decomposes into CO and benzoic acid, to a less degree into CO_2 and benzaldehyde. When mixed with benzene containing thiophene and sulphuric acid, it is colored deep red, afterward blue-violet; all its derivatives, and also, isatin, react similarly. Its *ethyl ester* boils at 252°.

Being a ketonic acid it (its esters) unites with sodium bisulphite. It combines with CNH, forming oxycyanides, $C_6H_5.C(OH)(CN).CO_2H$, from which phenyl tartronic acid is derived. Sodium amalgam converts it into mandelic acid, and hydriodic acid and phosphorus at 160° into alphatoluic acid. Hydroxylamine converts it into phenylisonitroso-acetic acid (p. 754). Phenylhydrazine forms a hydrazone with it (*Berichte*, 23, 1575).

o-**Nitrobenzoylformic Acid**, $C_6H_4(NO_2).CO.CO_2H$, is formed from *o*-nitrobenzoyl cyanide, by means of potassium cyanide, etc. It crystallizes with one molecule of water, and melts at 47°. It forms two isomeric hydrazones (*Berichte*, 23, 2080). When anhydrous it melts with decomposition at 122°. Ferrous sulphate and sodium hydroxide reduce it to—

o-**Amido-phenylglyoxylic Acid**, $C_6H_4(NH_2).CO.CO_2H$, Isatinic Acid. It is a white powder, obtained from its lead salt by hydrogen sulphide. Digestion of its solution converts it at once into its lactime—isatin, $C_8H_5NO_2$ (p. 755).

The lactam of isatinic acid,  $C_6H_4\left\langle\begin{matrix}CO.CO\\ \diagup \\ NH\end{matrix}\right.$ (p. 755), is unstable; the aceto-derivative, aceto-pseudo-isatin (see this), however, is stable. It dissolves in alkalies, forming salts of **Aceto-isatinic Acid**,  $C_6H_4\left\langle\begin{matrix}CO.CO_2H\\ NH.CO.CH_3\end{matrix}\right.$, from which the latter may be separated by dilute acids. The acid dissolves with difficulty in cold water, crystallizes from alcohol in needles, and melts at 160°. Boiling hydrochloric acid decomposes it with separation of isatin. When in an acetic acid solution it is reduced to aceto-*o*-amido mandelic acid by sodium amalgam (p. 774).

p-**Dimethylamido-phenylglyoxylic Acid**, $(CH_3)_2.N.C_6H_4.CO.CO_2H$, is produced from dimethyl aniline and chloroxalic ester (p. 601). It melts at 187°.

2. *p*-**Toluyl-formic Acid**, $C_9H_8O_3 = C_6H_4(CH_3).CO.CO_2H$, Tolylglyoxylic Acid, is obtained from toluene, chloroxalic ester and $AlCl_3$ (*Berichte*, 20, 2048), as well as by oxidizing *p*-methyl-tolyl ketone with potassium ferricyanide (*Berichte*, 20, 1763). It does not volatilize with steam. It crystallizes from an ethereal solution and melts about 96°. Its phenylhydrazine derivative melts at 144° Potassium permanganate oxidizes it to *p*-toluic and terephthalic acids. It yields *p*-tolyl-oxyacetic and *p* tolyl-acetic acids upon reduction (p. 757).

3. **Phenylpyroracemic Acid**, $C_9H_8O_3 = C_6H_5.CH_2.CO.CO_2H$, results from the union of phenyl-acetic ester and oxalic ester by the elimination of carbon dioxide from the phenyl-oxalacetic acid produced at first. It is identical with phenylglycidic acid, from benzoylimido-cinnamic acid (*Berichte*, 17, 1616) and phenyl-β-bromlactic acid. It dissolves with much difficulty in water, crystallizes

in brilliant leaflets, and melts at 154°. Ferric chloride imparts an intense green color to its solution. Its *phenylhydrazone* melts at 161°. Being an α-diketone, it yields a quinoxaline with *o*-toluylene diamine (*Berichte*, 20, 2465).

4. **Xylyl Glyoxylic Acids**, $C_{10}H_{10}O_3 = C_6H_3(CH_3)_2.CO.CO_2H$, result upon oxidizing xylylmethyl ketones (*Berichte*, 19, 230; 20, 1766).

β-Ketonic Acids.

In addition to the general reactions given upon p. 761, this class of acids may also be prepared by the action of the benzaldehydes upon diazoacetic esters (p. 374) (*Berichte*, 18, 2371):—

$$C_6H_5.COH + CHN_2.CO_2R = C_6H_5.CO.CH_2.CO_2R + N_2.$$

The β-ketonic-acids form pyrazole compounds with phenylhydrazine (p. 339).

1. **Benzoyl Acetic Acid**, $C_6H_5.CO.CH_2.CO_2H$. Its ethyl ester was first prepared by dissolving phenyl-propiolic ester in sulphuric acid and then diluting with water (p. 726) (*Berichte*, 16, 2128):—

$$C_6H_5.C:C.CO_2R + H_2O = C_6H_5.CO.CH_2.CO_2R.$$

It is also formed when benzaldehyde is heated with diazo-acetic ester, and by the action of sulphuric acid and water upon α-bromcinnamic ester (*Berichte*, 19, 1392). It is most conveniently made by the action of dry sodium ethylate or sodium upon ethyl benzoate and acetic ester (*Berichte*, 20, 653, 2179).

Small quantities of the ester are produced when esters of carbonic acid act upon acetophenone. Benzoylacetic ester is an oil with an odor resembling that of aceto-acetic ester. It boils at 265–270° with slight decomposition. The *free* acid is obtained by saponifying the ester at the ordinary temperature with potassium hydroxide. It dissolves with difficulty in water, very readily in alcohol and ether, and crystallizes in needles. When rapidly heated, these melt at 103-104°, decomposing into carbon dioxide and acetophenone. Boiling acids produce the same decomposition. Ferric chloride imparts a deep violet color to its aqueous solution.

Benzoyl-acetic ester unites with aniline, forming β-phenylamido-phenylacrylic ester, which yields α-phenyl-γ-oxyquinoline by condensation (*Berichte*, 21, 521).

Diazobenzene chloride converts benzoyl acetic ester into the phenylhydrazone of benzoyl-glyoxylic ester, $C_6H_5.CO.C(N_2H.C_6H_5).CO_2.C_2H_5$ (p. 652) (*Berichte*, 21, 2120).

The CH_2-group of benzoyl-acetic ester can be replaced by alkyls and radicals.

Methylbenzoyl-acetic Ester, $C_6H_5.CO.CH(CH_3).CO_2R$, when treated with nitrous acid eliminates the CO_2 group (p. 338) and forms α-isonitrosopropiophenone, $C_6H_5.CO.C(N.OH).CH_3$ (*Berichte*, 21, 2119).

Allyl-benzoyl-acetic Acid, $C_6H_5.CO.CH(C_3H_5).CO_2H$, is isomeric with benzoyl-tetramethylene carboxylic acid (p. 520) and melts at 122–125°.

***p*-Nitrobenzoyl-acetic Acid**, $C_6H_4(NO_2).CO.CH_2.CO_2H$, melts at 135°, and is produced in a manner analogous to that of benzoyl acetic acid, *i. e.*, by heating *p*-nitrophenyl propiolic ester, $C_6H_4(NO_2).C:C.CO_2R$, to 35° with sulphuric acid, while *o*-nitrophenyl propiolic ester is transposed into the isomeric isatogenic ester (*Berichte*, 17, 326). For additional derivatives see *Berichte*, 18, 951.

2. **Phenylaceto-acetic Acid**, $C_6H_5.CH{<}^{CO.CH_3}_{CO_2H}$. The ethyl ester of the dinitro-acid, $C_6H_3(NO_2)_2.CH(CO.CH_3).CO_2R$, is obtained from sodium aceto-acetic ester and *op*-dinitrobrombenzene. It forms yellow prisms, melting at 94° (*Berichte*, 21, 2470). The ester of the *trinitro acid* is obtained in a similar manner from picryl chloride. It melts at 98° (*Berichte*, 23, 2720). See *Berichte*, 22, 990, for the action of tribromdinitrobenzene.

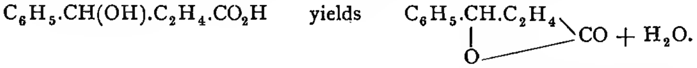
3. **Benzylaceto-acetic Acid**, $C_6H_5.CH_2.CH{<}^{CO.CH_3}_{CO_2H}$. Its ethyl ester is derived from aceto-acetic ester and benzyl chloride (p. 337). It boils at 276° and by the ketone decomposition yields benzyl acetone (p. 730); by the acid decomposition it forms phenylpropionic acid (p. 759).

Of the class of γ-ketonic acids may be mentioned:—

1. **Benzoylpropionic Acid**, $C_6H_5.CO.CH_2.CH_2.CO_2H$, which is obtained from benzene and succinic anhydride by means of $AlCl_3$:—

$$C_6H_6 + C_2H_4(CO)_2O = C_6H_5.CO.C_2H_4.CO_2H.$$

It is also formed by reducing benzoyl acrylic acid with HgNa; by the elimination of carbon dioxide from benzoylisosuccinic acid (p. 765), and from phenacyl-benzoyl-acetic ester by the ketone decomposition. It dissolves with difficulty in hot water, crystallizes in needles, and melts at 116°. Sodium amalgam reduces it to phenyl-γ-oxybutyric acid, which, upon the loss of water, becomes phenyl butyrolactone (*Berichte*, 15, 1890):—



$$C_6H_5.CH(OH).C_2H_4.CO_2H \quad \text{yields} \quad \begin{matrix}C_6H_5.CH.C_2H_4\\ |\qquad\quad \\ O\qquad\quad\end{matrix}{>}CO + H_2O.$$

Phosphorus pentasulphide converts the acid into phenyloxythiophene (*Berichte*, 19, 553).

The benzenes condense with other dibasic acid anhydrides, *e.g.*, maleïc and phthalic anhydrides (see benzoyl acrylic acid).

2. **Phenyl-lævulinic Acid**, $C_{11}H_{12}O_3 = C_6H_5.CH{<}^{CH_2.CO.CH_3}_{CO_2H}$, is derived from phenylacetosuccinic ester. Sodium amalgam converts it into a lactonic acid (*Berichte*, 18, 790).

3. **Acetobenzoic Acids**, $C_9H_8O_3 = C_6H_4{<}^{CO.CH_3}_{CO_2H}$, acetophenone carboxylic acids. The *ortho* form is produced upon heating benzoylaceto-carboxylic acid (from phthalyl acetic acid, p. 765) to 100°, or by boiling it with alkalies. It consists of flat needles, melting at 115°. Hydriodic acid reduces it to *o*-ethylbenzoic acid (p. 754). It unites with hydroxylamine and phenylhydrazine to form peculiar compounds. Two molecules of water are eliminated (*Berichte*, 19, 1996). *Trichlor-* and *Tribrom-acetophenone-Carboxylic Acid*, $C_6H_4(CO.CX_3)\,CO_2H$, are produced by the decomposition of the indene derivatives (*Berichte*, 21, 2396). The *para*-acid is prepared by oxidizing oxyisopropylbenzoic acid with a chromic acid mixture. It melts at 200°.

4. **Propionyl Benzoic Acids**, $C_6H_4{<}^{CO.C_2H_5}_{CO_2H}$, Propiophenone Carboxylic Acids. The *ortho*-form is produced when phthalyl propionic acid is boiled with alkalies. It melts at 58°. Hydriodic acid reduces it to *o*-propylbenzoic acid.

Diketonic Acids.

Benzoyl Glyoxylic Acid, $C_6H_5.CO.CO.CO_2H$. Its α-hydrazone is derived from benzoylacetic ester and diazobenzene chloride (p. 763).

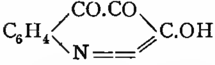
Benzoyl Pyroracemic Acid, $C_6H_5.CO.CH_2.CO.CO_2H + H_2O$, is produced from acetophenone and oxalic ester (p. 761). It melts at 43°. Ferric chloride imparts a blood-red color to it. The free acid melts about 157° with evolution of carbon dioxide, and is colored a deep blue by ferric chloride. Phenylhydrazine converts the ester into a pyrazole derivative (*Berichte*, 21, 1131).

When benzoyl chloride acts upon acetoacetic ester and benzoyl acetic ester it produces *benzoyl acetoacetic ester*, $C_6H_5.CO.CH.(CO.CH_3).CO_2R$ and *dibenzoyl-acetic ester*, $(C_6H_5.CO)_2.CH.CO_2R$. The former decomposes into acetophenone and benzoyl acetone (p. 731), while the latter yields acetophenone, benzoic acid and *dibenzoyl methane*, $(C_6H_5.CO)_2CH_2$, melting at 81° and boiling beyond 200°.

Bromacetophenone (p. 728) and acetoacetic ester yield *Acetophenone* (Phenacyl)-*acetoacetic Ester*, $\begin{matrix}CH_3.CO\\C_6H_5.CO.CH_2\end{matrix}\!\!>\!CH.CO_2R$.

This decomposes into acetophenone acetone, but by condensation (as a γ-diketone) forms methyl phenyl-furfurane carboxylic acid (p. 527). In the same manner benzoyl acetic ester yields *phenacyl-benzoylacetic ester*, $\begin{matrix}C_6H_5.CO\\C_6H_5.CO.CH_2\end{matrix}\!\!>\!CH.CO_2R$, which by decomposition forms benzoyl-propionic acid (p. 764) and *diphenacyl*, $(C_6H_5.CO.CH_2)_2$ (p. 731), and by condensation yields diphenyl-furfurane carboxylic acid (p. 524) (*Berichte*, 21, 3053).

Quinisatinic Acid, $C_6H_4\!<\!\begin{matrix}CO.CO.CO_2H\\NH_2\end{matrix}$, *o*-amido-phenyl mesoxalylic acid. It is obtained by oxidizing dioxycarbostyril with ferric chloride. From water it crystallizes in yellow prisms. Heated to 120° it becomes a lactime—quinisatin, This is analogous to the formation of isatin from isatinic acid (*Berichte*, 17, 985).



$$C_6H_4\!<\!\begin{matrix}CO.CO\\N=\!=\end{matrix}\!\!>\!C.OH$$

Diphenacylaceto-acetic Acid, $(C_6H_5.CO.CH_2)_2C.(CO.CH_3).CO_2H$ (*Berichte*, 22, 3225), is a triketonic acid.

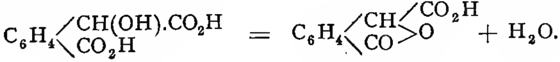
Dibasic Ketonic Acids.

Benzoyl chloride converts malonic esters into—

Benzoyl Malonic Ester, $C_6H_5.CO.CH(CO_2R)_2$ (*Berichte*, 20, Ref. 381). Its *o-nitro*-compound (obtained with *o*-nitrobenzoyl chloride) yields quinoline derivatives when reduced (*Berichte*, 22, 386).

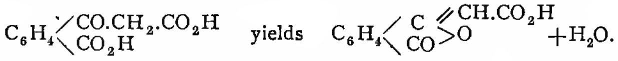
Benzoyl-isosuccinic Ester, $C_6H_5.CO.CH_2.CH(CO_2R)_2$ (*Berichte*, 19, 95), is obtained from bromacetophenone and malonic ester. The free acid melts at 180°, decomposing at the same time into carbon dioxide and benzoyl propionic acid (p. 764).

***o*-Carbophenyl glyoxylic Acid,** $C_6H_4\!<\!\begin{matrix}CO.CO_2H\\CO_2H\end{matrix}$, is formed by oxidizing hydrindene carboxylic acid and also α-naphthol with potassium permanganate (*Berichte*, 21, 1609). It is very readily soluble in water, melts at 140°, and decomposes into carbon dioxide and phthalic anhydride. Sodium amalgam reduces it to an oxy-acid, which immediately changes to its lactonic acid—phthalide carboxylic acid (p. 772):—



$$C_6H_4\!<\!\begin{matrix}CH(OH).CO_2H\\CO_2H\end{matrix} = C_6H_4\!<\!\begin{matrix}CH\!<\!\begin{matrix}CO_2H\\ \end{matrix}\\CO\end{matrix}\!\!>\!O + H_2O.$$

o-**Carbobenzoyl Acetic Acid,** $C_6H_4\Big<{}^{CO.CH_2.CO_2H}_{CO_2H}$, Benzoyl aceto-carboxylic acid. This acid is formed when phthalyl acetic acid is dissolved in alkalies. It crystallizes in brilliant needles, melting at 90°, with decomposition into carbon dioxide and *o*-acetobenzoic acid (p. 764). When this acid is dissolved in sulphuric acid and precipitated with water it reverts again to phthalyl acetic acid; a ketonic acid is transposed into a lactone (p. 352) (*Berichte*, 17, 2619):—



$$C_6H_4\Big<{}^{CO.CH_2.CO_2H}_{CO_2H} \quad \text{yields} \quad C_6H_4\Big<{}^{C=CH.CO_2H}_{CO}\Big>O + H_2O.$$

Consult *Berichte*, 17, 2665; 19, 3144 for different diketone-dicarboxylic acids.

MONOBASIC OXY-ACIDS.

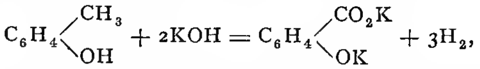
The aromatic oxy-acids containing hydroxyl united to the benzene nucleus, *e. g.*, $C_6H_4.OH.CO_2H$, combine the character of acids and phenols, hence are designated *Phenol acids.* Should the hydroxyl groups enter the side-chains, we would obtain aromatic oxy-acids (alcohol acids), corresponding in all particulars to the oxy-fatty acids.

The phenol-acids are produced:—

1. From the benzene carboxylic acids by methods analogous to those used in the preparation of the phenols from the benzenes: the conversion of the amido-acids, by means of nitrous acid, into diazo-compounds and then boiling the latter with water; by fusing the sulphobenzoic acids with alkalies. The haloid benzene carboxylic acids react like the sulpho-acids when subjected to similar treatment (p. 666):—

$$C_6H_4Cl.CO_2H + KOH = C_6H_4(OH).CO_2H + KCl.$$

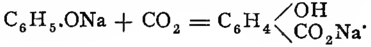
The homologous phenols become oxy-acids when fused with alkalies:—



$$C_6H_4\Big<{}^{CH_3}_{OH} + 2KOH = C_6H_4\Big<{}^{CO_2K}_{OK} + 3H_2,$$

whereas they are only oxidized by the ordinary oxidizing agents after the hydroxyl hydrogen has been replaced by alkyls or acid radicals (p. 686). The oxy-aldehydes that are oxidized with difficulty are readily changed to oxy-acids upon fusion with the alkalies.

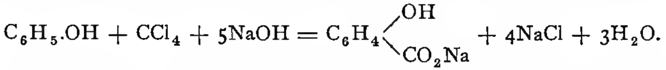
2. The oxy-acids are produced synthetically by the action of chlorcarbonic esters or carbon dioxide upon the sodium salts of the phenols (p. 739):—



$$C_6H_5.ONa + CO_2 = C_6H_4\Big<{}^{OH}_{CO_2Na}.$$

At lower temperatures (below 100°) phenol carbonates constitute the chief product. At more elevated temperatures these are re-arranged into their isomeric oxy-acids (p. 670). When this occurs the carboxyl-group generally enters the *ortho*-position. The polyhydric phenols are often converted into oxy-acids by merely heating them together with ammonium or potassium carbonate (p. 739.)

3. A specifically synthetic method for the preparation of oxy-acids consists in the transposition of phenols by boiling them with carbon tetrachloride and caustic potash (*Berichte*, **10**, 2185):—

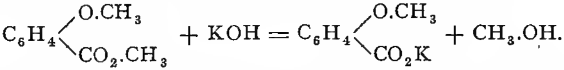


$$C_6H_5.OH + CCl_4 + 5NaOH = C_6H_4\left\langle\begin{matrix}OH\\CO_2Na\end{matrix}\right. + 4NaCl + 3H_2O.$$

This reaction is perfectly analogous to that of the formation of oxyaldehydes by means of chloroform (p. 723). As a general thing the carboxyl-group enters the ortho- or para-position, with the formation of two isomeric oxy-acids.

Their basicity is determined by the number of carboxyl groups present, as alkaline carbonates convert them into carboxyl salts.

Their hydroxyl hydrogen can also be replaced by alkalies, forming *basic* salts, *e. g.*, $C_6H_4\left\langle\begin{matrix}ONa\\CO_2Na\end{matrix}\right.$. Carbon dioxide, however, will convert the latter into *neutral* salts. The ethers or esters manifest a like deportment, inasmuch as it is only the carboxyl esters that are saponified by alkalies (p. 349):—



$$C_6H_4\left\langle\begin{matrix}O.CH_3\\CO_2.CH_3\end{matrix}\right. + KOH = C_6H_4\left\langle\begin{matrix}O.CH_3\\CO_2K\end{matrix}\right. + CH_3.OH.$$

The ortho-oxy-acids, unlike the meta- and para-derivatives, volatilize in aqueous vapor, are colored violet by ferric chloride, and dissolve in chloroform. The meta-oxy-acids are colored reddish brown when heated with concentrated sulphuric acid, with the formation of oxyanthraquinones (*Berichte*, **18**, 2142). They are usually more stable than the ortho- and para-acids. Boiling concentrated hydrochloric acid decomposes the para-acids into carbon dioxide and phenols. Consult *Berichte*, **18**, Ref. 487 for the heat of neutralization of the three oxybenzoic acids. All the oxy-acids decompose into carbon dioxide and phenols when distilled with lime (p. 667).

Alcohol acids (p. 766) are perfectly analogous to the acids of the paraffin series in their modes of formation and properties.

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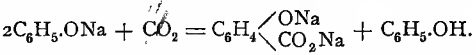
1. **Acids**, $C_7H_6O_3 = C_6H_4\left\langle\begin{matrix}CO_2H\\OH\end{matrix}\right.$, Oxybenzoic Acids.

1. **Ortho-oxybenzoic Acid**, $C_6H_4(OH).CO_2H(1, 2)$, **Salicylic Acid**, occurs in a free condition in the buds of *Spiræa ulmaria*, as the methyl ester in oil of *Gaultheria procumbens* (Oil of Wintergreen) and other varieties of gaultheria, from which it may be

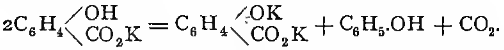
easily obtained by saponification with potassium hydroxide. It is prepared artificially: by oxidizing saligenin and salicylic aldehyde; by action of nitrous acid upon anthranilic acid; from the two nitro-(1, 3)-brombenzoic acids (p. 748); by fusing orthochlor- and brombenzoic acids, orthotoluene sulphonic acid and ortho-cresol with alkalies; from phenol with CO_2, or with chlorcarbonic ester and sodium, or by means of CCl_4, and sodium hydroxide (p. 767). Its production from CO_2 and sodium phenoxide is especially interesting. This reaction is employed for its formation upon a large scale. The acid can be made according to two methods:—

(*a*) When sodium phenoxide is heated in a current of carbon dioxide at 180–220°, the latter is absorbed, half of the phenol distils over, and the residue is disodium salicylate—Kolbe:—



$$2C_6H_5.ONa + CO_2 = C_6H_4\left\langle\begin{matrix}ONa\\CO_2Na\end{matrix}\right. + C_6H_5.OH.$$

The same reaction occurs when potassium phenoxide is heated to 150° in a current of carbon dioxide. At a more elevated temperature, however, there is formed with the dipotassium salicylate its isomeride, dipotassium paraoxybenzoate. The latter is more abundant in proportion to the increased temperature, until at 220° it is the sole product. Primary potassium salicylate undergoes a similar transposition at 220°; phenol then distils over and dipotassium paraoxybenzoate constitutes the residue:—



$$2C_6H_4\left\langle\begin{matrix}OH\\CO_2K\end{matrix}\right. = C_6H_4\left\langle\begin{matrix}OK\\CO_2K\end{matrix}\right. + C_6H_5.OH + CO_2.$$

The sodium salt also decomposes in this manner, but instead of paroxybenzoic acid it yields disodium salicylate. On the other hand, if we expose primary sodium paraoxybenzoate, at 280–290°, in a current of CO_2, there results conversely (together with phenol) disodium salicylate. This strikingly illustrates the different deportment of potassium and sodium on fusion (*Jour. pr. Ch.* [2], 10, 95; 16, 425).

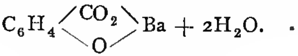
(*b*) Sodium phenoxide is saturated under pressure, in closed vessels, with carbon dioxide, when it is converted into sodium phenocarbonate, $C_6H_5.O.CO_2Na$ (p. 670). By continuing the pressure and applying a heat of 120–130°, this salt is changed to sodium salicylate, $C_6H_4(OH).CO_2Na$. In this manner all the phenol is converted into salicylic acid (R. Schmitt, *Berichte*, **18**, Ref. 439).

(*c*) A third procedure less adapted for the production of salicylic acid, consists in heating phenol carbonate (p. 670) at 200°, with caustic soda. Phenol distils over and sodium salicylate remains:—

$$(C_6H_5.O)_2CO + NaOH = C_6H_4(OH).CO_2Na + C_6H_5.OH$$

Salicylic acid consists of four-sided prisms and crystallizes readily from hot water in long needles. It dissolves in 400 parts water at 15°, and in 12 parts at 100°; it is very soluble in chloroform. It melts at 155–156°, and when carefully heated sublimes in needles; when quickly heated (or with water at 220°, more readily with hydrochloric acid) it breaks up into carbon dioxide and phenol. Its aqueous solution acquires a violet coloration upon the addition of ferric chloride. It is a powerful antiseptic, hence its wide application.

When salicylic acid is heated with baryta water, the hydrogen atoms of both hydroxyls are replaced by barium, and leaflets of the basic salt separate:—



$$C_6H_4\left\langle\begin{matrix}CO_2\\O\end{matrix}\right\rangle Ba + 2H_2O.$$

When boiled with lime water the basic calcium salt is precipitated as an insoluble powder. This behavior affords a means of separating salicylic from the other two oxybenzoic acids. The halogens react readily with salicylic acid, yielding substitution products. Nitration produces three nitro-salicylic acids.

PCl_5 converts salicylic acid into the *chloride*, $C_6H_4Cl.COCl$,—an oil, boiling at 240°. Hot water converts it into orthochlorbenzoic acid.

PCl_3O produces the so-called *salicylide*, $C_7H_4O_2 = C_6H_4\left\langle\begin{matrix}CO\\O\end{matrix}\right\rangle$ (?), which crystallizes in shining leaflets, melting at 195°. Boiling alkalies change it again to salicylic acid.

The *esters* of salicylic acid appear, according to the common method, by conducting hydrochloric acid gas into its alcoholic solutions. The *methyl ester*, $C_6H_4(OH).CO_2.CH_3$, is the chief ingredient of wintergreen oil (from *Gaultheria procumbens*). It is an agreeably-smelling liquid, which boils at 224° (corrected); its sp. gr. = 1.197 at 0°. It dissolves in alkalies, forming unstable phenol salts. Ferric chloride gives it a violet coloration. The *ethyl ester*, $C_6H_4(OH)CO_2.C_2H_5$, boils at 223°.

When the methyl ester is digested with an alcoholic solution of potassium hydroxide and methyl iodide at 120° (p. 670), we get the *dimethyl ester*, $C_6H_5.\left\langle\begin{matrix}O\,CH_3\\CO_2.CH_3\end{matrix}\right.$, which is an oil boiling at 245°. Boiled with potassium hydroxide, it is saponified, yielding methyl alcohol and methyl salicylic acid, $C_6H_4\left\langle\begin{matrix}O.CH_3\\CO_2H\end{matrix}\right.$, which forms large plates, melting at 98°. It is readily soluble in hot water and alcohol. It decomposes into carbon dioxide and anisol, $C_6H_5.O.CH_3$, when heated to 200°.

We can produce *salicylic-diethyl ester*, boiling at 259°, and *ethylsalicylic acid* in the same manner. The latter melts at 19.5°, and at 300° decomposes into carbon dioxide, and ethyl phenol, $C_6H_5.O.C_2H_5$.

Acetyl chloride converts salicylic acid into aceto-salicylic acid, $C_6H_4(O.C_2H_3O).CO_2H$, which crystallizes in delicate needles, and melts at 218°.

The phenol salicylic esters are the *salols*, used as antiseptics. They are produced when $POCl_3$ or PCl_5 acts upon a mixture of salicylic acid and various phenols. Or phosgene may be allowed to act upon a mixture of the sodium salts. In this way a great variety of different salols has been obtained (*Berichte*, 21, Ref. 554; 22, Ref. 309).

Salicylic Phenol Ester, $C_6H_4(OH).CO_2.C_6H_6$, *Salol*, consists of white crystals, melting at 43°. When sodium salol, $C_6H_4(ONa).CO_2.C_2H_6$ (from salol and sodium), is heated to 280°–300°, it changes to the isomeric sodium salt of *phenyl-salicylic acid*, $C_6H_4(O.C_6H_6).CO_2H$, which melts at 113°, and is not colored by ferric chloride (*Berichte*, 21, 502; 23, Ref. 342). It changes to diphenylene ketonoxide, $C_6H_4\begin{smallmatrix}\diagup O \diagdown\\ \diagdown CO \diagup\end{smallmatrix}C_6H_4$ (Xanthone), by the elimination of water (by means of sulphuric acid, or upon heating with PCl_3).

2. **Meta-oxybenzoic Acid**, $C_6H_4\begin{smallmatrix}\diagup OH\\ \diagdown CO_2H\end{smallmatrix}$ (1, 3), is produced: by acting with nitrous acid upon ordinary (1, 3)-amidobenzoic acid; by fusing (1, 3)-chlor-, brom-, iodo-, and sulpho-benzoic acids and metacresol with potassium hydroxide. It also results from metacyanphenol. It usually crystallizes in wart-like masses consisting of microscopic leaflets, dissolves in 260 parts of water at 0°, and readily in hot water. It melts at 200°, and sublimes without decomposition. Ferric chloride does not color it. It yields carbon dioxide and phenol when heated with alkalies.

The *ethyl ester*, $C_6H_4(OH).CO_2.C_2H_5$, crystallizes in plates, soluble in hot water, and melting at 72°. It boils at 282°. The *dimethyl ester*, $C_6H_4(O.CH_3).CO_2.CH_3$, is formed when metaoxybenzoic acid is heated with methyl iodide (2 molecules) and potassium hydroxide (2 molecules) to 140°. Boiling caustic potash converts this into *methyl-metaoxybenzoic acid*, $C_6H_4(O.CH_3).CO_2H$. The latter is also obtained from the methyl ether of metabromphenol, $C_6H_4Br.O.CH_3$, with sodium and carbon dioxide. It crystallizes in shining scales, is easily soluble in water, melts at 107°, and sublimes undecomposed.

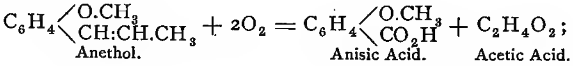
3. **Para-oxybenzoic Acid**, $C_6H_4\begin{smallmatrix}\diagup OH\\ \diagdown CO_2H\end{smallmatrix}$ (1, 4), is obtained from parachlor-, brom-, iodo- and sulpho-benzoic acids, and also from many resins, by fusing them with potassium hydroxide. It results, too, when para-amidobenzoic acid is treated with nitrous acid or phenol with carbon tetrachloride and sodium hydroxide (together with salicylic acid). An interesting way of obtaining it consists in heating potassium phenoxide in a current of carbon dioxide (p. 768) at 220°. This is the best course to pursue in preparing it (*Journal pract. Chemie*, 16, 36, *Berichte*, 22, Ref. 622).

Paraoxybenzoic acid crystallizes from water in monoclinic prisms, containing 1 molecule of H_2O. This it loses at 100°. It is somewhat more easily soluble than salicylic acid (in 580 parts H_2O at 0°), and melts at 210° with partial decomposition into carbon dioxide and phenol. Ferric chloride does not color it, but throws down a yellow precipitate which dissolves in an excess of the reagent. Its basic *barium salt*, $C_6H_4\begin{smallmatrix}\diagup O \diagdown\\ \diagdown CO_2 \diagup\end{smallmatrix}Ba$, is insoluble, and may be employed to separate the acid from its meta-isomeride.

The *methyl ester*, $C_6H_4\begin{smallmatrix}\diagup OH\\ \diagdown CO_2.CH_3\end{smallmatrix}$, consists of large plates, melting at 17°, and distilling at 273°. The *ethyl ester* melts at 113°, and boils near 297°.

Methyl-paraoxybenzoic Acid, $C_6H_4\begin{smallmatrix}\diagup O.CH_3\\ \diagdown CO_2H\end{smallmatrix}$, and *ethyl-paraoxybenzoic acid*, $C_6H_4\begin{smallmatrix}\diagup O.C_2H_5\\ \diagdown CO_2H\end{smallmatrix}$, are produced the same as the corresponding compounds of the other two benzoic acids; the second melts at 195°.

Anisic Acid, called methyl paraoxybenzoic acid, is obtained by oxidizing anisol and anethol (p. 724) with nitric acid or a chromic acid mixture:—



$$\underset{\text{Anethol.}}{C_6H_4\begin{smallmatrix}\diagup O.CH_3\\ \diagdown CH{:}CH.CH_3\end{smallmatrix}} + 2O_2 = \underset{\text{Anisic Acid.}}{C_6H_4\begin{smallmatrix}\diagup O.CH_3\\ \diagdown CO_2H\end{smallmatrix}} + \underset{\text{Acetic Acid.}}{C_2H_4O_2};$$

or by oxidizing the methyl ether of *p*-cresol, $C_6H_4<\begin{matrix}O.CH_3\\CH_3\end{matrix}$. It is prepared by oxidizing anisol with a chromic acid mixture (*Annalen*, **141**, 248).

Anisic acid crystallizes from hot water in long needles, from alcohol in rhombic prisms, melts at 185°, sublimes and boils without decomposition at 280°. Heated with baryta it breaks up into carbon dioxide and anisol, $C_6H_5.O.CH_3$. It yields paraoxybenzoic acid when heated with hydrochloric or hydriodic acid (p. 668). The salts of anisic acid are very soluble in water and crystallize well. The halogens and nitric acid afford substitution products. These yield substituted anisols by distillation with baryta.

Acids, $C_8H_8O_3$.

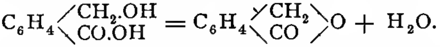
1. **Oxytoluic Acids**, $C_6H_3(CH)_3<\begin{matrix}OH\\CO_2H\end{matrix}$, **Cresotinic Acids**. The ten possible isomerides are known (*Berichte*, **16**, 1966). They result from the toluic acids, $C_6H_4.CH_3.COOH$, by the substitution of OH for one atom of hydrogen in the benzene nucleus, and from the cresols, $C_6H_4(CH_3).OH$, by the introduction of CO_2H, by means of sodium and carbon dioxide, or by the carbon chloride reaction (p. 767). They can also be obtained by the oxidation (fusion with caustic alkali) of their aldehydes, $C_6H_3(CH_3)(OH).CHO$. The latter are made from the cresols by means of the chloroform reaction. Those isomerides in which the *OH* occupies the ortho place with reference to the CO_2H group (4 isomerides) are, like salicylic acid, colored intensely *violet* by ferric chloride, are readily soluble in cold chloroform, and are volatile in steam. When ignited with lime the oxytoluic acids split up into carbon dioxide, and the corresponding cresols, $C_6H_4(CH_3).OH$. Some of them, especially the ortho-oxyacids, suffer this change when heated with concentrated hydrochloric acid to 200°. Symmetrical *metaoxy-m-toluic acid*, yields, by nitration, a trinitro-product, $C_6(OH)(NO_2)_3<\begin{matrix}CH_3\\CO_2H\end{matrix}$, melting at 180°; this is identical with the *nitrococcic acid* obtained from aloes (*Berichte*, **18**, 251).

2. **Oxyphenyl Acetic Acids**, $C_6H_4<\begin{matrix}OH\\CH_2.CO_2H\end{matrix}$, oxy-alphatoluic acids. The *p*- and *m*-acids can be obtained from the corresponding amidophenyl acetic acids, $C_6H_4(NH_2).CH_2.CO_2H$ (p. 756), by diazotizing, and also from the oxybenzyl cyanides, $C_6H_4(OH).CH_2CN$ (p. 735).

o-Oxyphenyl Acetic Acid has been obtained from isatinic acid (and isatin), (p. 762). The diazotizing of isatin at first produces oxyphenylglyoxylic acid, $C_6H_4(OH).CO.CO_2H$, which by action of sodium amalgam becomes *o*-oxymandelic acid, $C_6H_4(OH).CH(OH).CO_2H$. The latter on boiling with hydriodic acid yields *o*-oxy-phenylacetic acid, melting at 137°. Ferric chloride colors it violet. Being a γ-oxyacid it forms a *lactone*, $C_6H_4<\begin{matrix}O\diagdown\\CH_2.CO\end{matrix}$, when distilled. This melts at 49°, and boils at 236° (*Berichte*, **17**, 975).

m-Oxyphenyl Acetic Acid melts at 129°. *p-Oxyphenyl Acetic Acid* occurs in urine, and arises from the decomposition of albuminous bodies. It crystallizes in flat needles, melts at 148°, and is colored dirty-green by ferric chloride. When distilled with lime it yields carbon dioxide, and *p*-cresol, $C_6H_4(CH_3).OH$.

3. **Oxymethylbenzoic Acids,** $C_6H_4\left\langle\begin{matrix}CH_2.OH\\CO_2H\end{matrix}\right.$. Mineral acids precipitate the *ortho* acid from its salts (obtained by boiling phthalide with alkalies) in the form of a powder. This melts at 118°, with decomposition into water and phthalide. It is a γ-oxyacid, hence by the elimination of water can yield a lactone (even by boiling with water):—



$$C_6H_4\left\langle\begin{matrix}CH_2.OH\\CO.OH\end{matrix}\right. = C_6H_4\left\langle\begin{matrix}CH_2\\CO\end{matrix}\right\rangle O + H_2O.$$

The lactone, $C_8H_6O_2$, called **Phthalide,** is prepared by the action of hydriodic acid, or zinc and HCl upon phthalic chloride, $C_6H_4\left\langle\begin{matrix}CCl_2\\CO-\end{matrix}\right\rangle O$ (*Berichte*, 10, 1445). It also results from orthoxylylene chloride upon boiling with water and lead nitrate; by the reduction of phthalic anhydride in acetic acid solution with zinc dust (*Berichte*, 17, 2178); by the action of bromine vapor upon orthotoluic acid at 140°, and most easily by digesting phthalidin, C_8H_7NO (from phthalimide) with caustic soda (*Berichte*, 17, 2598). Phthalide resembles the lactones perfectly and is the first discovered member of that series. It crystallizes from hot water and alcohol, in needles or plates, melts at 73°, and boils at 290° (cor.). It is reduced to orthotoluic acid on boiling with hydriodic acid. Potassium permanganate oxidizes it to phthalic acid. Sodium amalgam reduces it to *hydrophthalide*, $C_6H_4\left\langle\begin{matrix}CH_2\\CH(OH)\end{matrix}\right\rangle O$. The esters of benzoic acid are similarly reduced (*Berichte*, 11, 239).

Phthalide yields the base **Phthalidin,** $C_8H_7NO = C_6H_4\left\langle\begin{matrix}CH_2-\\C(NH)\end{matrix}\right\rangle O$, or $C_6H_4\left\langle\begin{matrix}CH_2\\CO\end{matrix}\right\rangle NH$, when it is heated in an atmosphere of ammonia. Phthalidin can also be very readily obtained by reducing phthalimide with tin and hydrochloric acid. It crystallizes from hot water in needles, melting at 150° and distilling at 337°.

Dialkylphthalides, *e.g*, $C_6H_4\left\langle\begin{matrix}C(CH_3)_2\\CO\end{matrix}\right\rangle O$, have been obtained by the action of zinc and alkyl iodides upon phthalic anhydride (*Berichte*, 22, Ref. 11).

The potassium salt of *cyan-benzyl-o-carboxylic acid* = (cyan-*o*-toluic acid) is formed when phthalide and potassium cyanide are heated to 180°:—

$$C_6H_4\left\langle\begin{matrix}CH_2\\CO\end{matrix}\right\rangle O + CNK = C_6H_4\left\langle\begin{matrix}CH_2CN\\CO_2K\end{matrix}\right. .$$

The free acid is a powder that is almost insoluble in water, and melts at 116°, without decomposition (*Berichte*, 19, Ref. 439).

Other phthalide derivatives worthy of note are phthalide-acetic acid, phenylphthalide, methylene phthalide, benzylidene phthalide, and the phthalides and phthaleïns.

4. **Phenylglycollic Acid, Mandelic Acid,** $C_6H_5.CH(OH).CO_2H$, was first obtained by heating amygdalin (p. 717) with hydrochloric acid, and is synthetically formed from benzaldehyde by the action of prussic acid and hydrochloric acid, and the transformation of the oxycyanide first produced:—

$$C_6H_5.CH(OH).CN + 2H_2O = C_6H_5.CH(OH).CO_2H + NH_3.$$

It can also be obtained from benzoylformic acid (p. 762), by reduction with sodium amalgam, and from phenylchloracetic acid (p. 754) by boiling it with alkalies, as well as by the action of alkalies upon dibromacetophenone, $C_6H_5.CO.CHBr_2$, or phenylglyoxal (p. 730).

Preparation.—Boil the oxycyanides either with concentrated hydrochloric acid or heat them with sulphuric acid, which has been diluted with one-half volume of water. Or the oxycyanide can be changed to phenylchloracetic acid by heating it to 140° with concentrated hydrochloric acid (*Berichte*, 14, 239). The *oxycyanide*, C_6H_5 CH(OH).CN, is obtained by digesting benzaldehyde for some time with 20 per cent. prussic acid (p. 347), or by gradually adding concentrated hydrochloric acid (1 molecule), with constant stirring, to a cooled mixture of benzaldehyde with ether and pulverized CNK (1 molecule).—*Berichte*, 14, 239 and 1965. The oxycyanide is a yellow oil with an odor resembling that of prussic acid and oil of bitter almonds. It solidifies at —10°, and decomposes when heated.

The natural mandelic acid, obtained from amygdalin, is optically active, and, indeed, lævo-rotatory. It forms brilliant crystals, melting at 132.8°. Synthetic-mandelic acid, called *paramandelic acid*, is optically inactive; it crystallizes in rhombic plates or prisms, and melts at 118°. It is more soluble in water than the lævo-acid (100 parts water at 20° dissolve 15.9 parts of the former and 8.6 parts of the latter). Both acids manifest like chemical deportment (like the tartaric acids, etc.). Dilute nitric acid converts them into benzoyl-formic acid, while by more powerful oxidation, they yield benzoic acid. When heated with hydriodic acid they form phenyl-acetic acid, with hydrobromic and hydrochloric acid chlorphenyl or bromphenyl acetic acids.

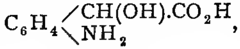
Inactive or para-mandelic acid, like racemic acid, consists of *dextro-* and *lævo-*mandelic acids (p. 64). Fermentation with *Penicillium glaucum* destroys the lævo and there remains the dextro-acid, which, so far as physical properties are concerned, resembles the so-called natural lævo-acid perfectly, only excepting the fact that the former rotates the plane equally as much to the right. Lævo-mandelic acid, however, is formed from the para-acid through the influence of a *schizomycetes* (Vibrio?) (*Berichte*, 17, 2723). The direct splitting up of para-mandelic acid into the dextro- and lævo-acids can be brought about by the crystallization of the cinchonine salt. The mixing together of the dextro- and lævo-acids (molecular quantities) results in the formation of inactive paramandelic acid. When the dextro- or lævo-acid is heated in a tube to 160° it is converted into the inactive mandelic acid.

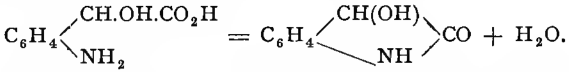
Nitro-mandelic Acids.

o-**Nitro-mandelic Acid**, $C_6H_4(NO_2).CH(OH).CO_2H$, is produced (analogous to mandelic acid) by dissolving *o*-nitro-acetophenone-dibromide, $C_6H_4(NO_2).CO.CHBr_2$, in caustic potash. It melts at 140°. When reduced with tin and hydrochloric acid it yields *o*-amido-mandelic acid, *i. e.*, dioxinol (see below) (*Berichte*, 20, 2203).

m-**Nitro-mandelic Acid** is obtained from *m*-nitrobenzaldehyde.

Amido-mandelic Acids.

o-**Amido-mandelic Acid**,  $C_6H_4\left\langle\begin{matrix}CH(OH).CO_2H\\NH_2\end{matrix}\right.$, Hydrindic Acid. Its sodium salt is formed from isatin by the action of sodium amalgam, and separates from the concentrated solution in brilliant crystals, $C_8H_8NaNO_3 + H_2O$. This is not stable in a free condition, but immediately passes into its lactam, dioxindol, by the splitting-off of water (p. 755):—



$$C_6H_4\left\langle\begin{matrix}CH.OH.CO_2H\\NH_2\end{matrix}\right. = C_6H_4\left\langle\begin{matrix}CH(OH)\\NH\end{matrix}\right\rangle CO + H_2O.$$

A more stable compound than the preceding is **Aceto-*o*-amidomandelic Acid**, $C_6H_4\left\langle\begin{matrix}CH(OH).CO_2H\\NH.CO.CH_3\end{matrix}\right.$. This is obtained from aceto-isatinic acid (p. 762) by the action of NaHg, and from aceto-dioxindol by its solution in baryta water. It is very soluble in water, crystallizes in needles, and melts at 142°. The action of hydriodic acid or sodium amalgam causes it to break up into acetic acid and oxindol, the anhydride of *o*-amido-phenyl acetic acid (p. 756).

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3. *Acids*, $C_9H_{10}O_3$.

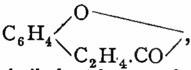
1. **Oxyethylbenzoic Acid**, $C_6H_4\left\langle\begin{matrix}CH(OH).CH_3\\CO_2H\end{matrix}\right.$ (ortho), is formed from acetophenone-carboxylic acid (p. 764) when treated with sodium amalgam. It yields a lactone which solidifies below 0° (*Berichte*, 10, 2205).

2. **Oxymesitylenic Acid**, $C_6H_2(CH_3)_2\left\langle\begin{matrix}OH\\CO_2H\end{matrix}\right.$ $(CO_2H:OH = 1:2)$, is obtained by fusing mesitylene sulphonic acid with caustic alkali, and when nitrous acid acts upon amidomesitylenic acid. It melts at 179°, and being an oxyacid is colored a deep blue by ferric chloride.

3. Oxyphenylpropionic Acids, $C_6H_4\left\langle\begin{matrix}OH\\C_2H_4.CO_2H\end{matrix}\right.$. There are six isomerides.

o-**Hydro-coumaric Acid, Melilotic Acid**, $C_6H_4\left\langle\begin{matrix}OH\\CH_2.CH_2.CO_2H\end{matrix}\right.$ (1, 2), occurs free and in combination with coumarin in the yellow melilot (*Melilotus officinalis*), and is produced by the action of sodium amalgam upon coumaric acid and coumarin (see this):—

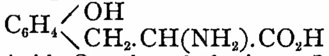
$$\underset{\text{Coumarin.}}{C_9H_6O_2} + H_2O + H_2 = C_9H_{10}O_3.$$

It crystallizes in long needles, dissolves easily in hot water, and melts at 81°. Ferric chloride imparts a bluish color to the solution. When distilled it passes into the *δ-lactone*, $C_9H_8O_2 =$  $C_6H_4\left\langle\begin{matrix}O\\C_2H_4.CO\end{matrix}\right\rangle$, *Hydrocoumarin*, melting at 25°, and boiling at 272°. When boiled with water it regenerates the acid. Melilotic acid decomposes when fused with alkali into salicylic acid and acetic acid; hence it is a benzene derivative of the ortho-series. *Ethyl Melilotic Acid*, $C_6H_4(O.C_2H_5).C_2H_4.CO_2H$, is produced by ethylating the acid and when sodium amalgam acts upon ethyl coumaric and ethyl coumarinic acids; it melts at 80°.

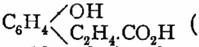
m-**Hydro-coumaric Acid**, $C_6H_4\left\langle\begin{matrix}OH\\CH_2.CH_2.CO_2H\end{matrix}\right.$ (1, 3), is obtained from meta-coumaric acid by means of sodium amalgam; it melts at 111°.

p-**Hydro-coumaric Acid**, $C_6H_4\left\langle\begin{matrix}OH\\CH_2.CH_2.CO_2H\end{matrix}\right.$ (1, 4), results when sodium amalgam acts upon para-coumaric acid, or when nitrous acid acts on *p*-amidohydrocinnamic acid (p. 758), and in the decay of tyrosine. It is very soluble in hot water, forms small crystals, and melts at 128° (*Berichte*, 17, Ref. 433).

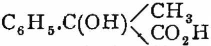
One of the amido-derivatives of *p*-hydro-coumaric acid is

Tyrosine, $C_9H_{11}NO_3$ =  $C_6H_4{<}\begin{matrix}OH\\ CH_2.CH(NH_2).CO_2H\end{matrix}$ (1, 4), Oxyphenyl-*α*-amidopropionic Acid, Oxyphenyl-alanine. It occurs in the liver, the spleen, the pancreas, and in stale cheese (*τυρὸς*), and is formed from animal substances, (albumen, horn, hair) on boiling them with hydrochloric or sulphuric acid; by fusion with alkalies or by putrefaction (together with leucine, aspartic acid, etc.). It may be prepared synthetically from *p*-amido-phenylalanine (from phenylacetaldehyde, p. 758) by the action of 1 molecule of potassium nitrite upon the hydrochloric acid salt. It is soluble in 150 parts boiling water, and crystallizes in delicate, silky needles; it dissolves with difficulty in alcohol, and is insoluble in ether.

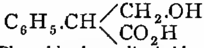
Mercuric nitrate produces a yellow precipitate, which becomes dark red in color if it be boiled with fuming nitric acid to which considerable water has been added (delicate reaction). Being an amido-acid, tyrosine unites with acids and bases, forming salts. If it be heated to 270° it decomposes into carbon dioxide and oxyphenylethylamine, $C_6H_4(OH).CH_2.CH_2.NH_2$. When fused with caustic potash it yields paraoxybenzoic acid, ammonia and acetic acid. Putrefaction causes the formation of hydroparacoumaric acid, and nitrous acid converts the tyrosine into para-oxyphenyl-lactic acid, $C_6H_4(OH).CH_2.CH(OH).CO_2H$ (*Annalen*, 219, 226).

Phloretic Acid,  $C_6H_4{<}\begin{matrix}OH\\ C_2H_4.CO_2H\end{matrix}$ (1, 4), oxyphenyl-*α*-propionic acid, is formed together with phloroglucin when phloretine is digested with potassium hydroxide (p. 695). It crystallizes in long prisms, is very soluble in hot water, and melts at 128–130°. Ferric chloride colors its solution green. Baryta decomposes it into carbon dioxide and ethyl phenol; fusion with potassium hydroxide produces paraoxybenzoic and acetic acids. The oxidation of methyl phloretic acid yields anisic acid. Phloretic acid, like the cresols, cannot be directly oxidized (p. 686).

4. **Phenyloxypropionic Acids**, $C_6H_5.C_2H_3(OH).CO_2H$. There are four isomerides:—

1.  $C_6H_5.C(OH){<}\begin{matrix}CH_3\\ CO_2H\end{matrix}$

α-Phenyl-lactic Acid,
Atrolactinic Acid.

2.  $C_6H_5.CH{<}\begin{matrix}CH_2.OH\\ CO_2H\end{matrix}$

α-Phenyl-hydracrylic Acid,
Tropic Acid.

3. $C_6H_5.CH_2.CH(OH).CO_2H$

β-Phenyl-lactic Acid.

4. $C_6H_5.CH(OH).CH_2.CO_2H$.

β-Phenyl-hydracrylic Acid.

(1) The so-called **Atrolactinic Acid** is obtained from *α*-bromhydro-atropic acid (p. 759), when the latter is boiled with a soda solution, and by oxidizing hydro-atropic acid with potassium permanganate. It is prepared synthetically from acetophenone, $C_6H_5.CO.CH_3$, by means of prussic acid and sulphuric acid or dilute hydrochloric acid, and by boiling the cyanide with concentrated hydrochloric acid we get *β-Chlorhydro-atropic Acid* (p. 759) (*Berichte*, 14, 1352 and 1980).

It dissolves very readily in water, crystallizes with one-half molecule of water in needles or plates, and at 80–85° loses its water of crystallization. While yet containing water it melts at 91°; when anhydrous at 93°. It remains unaltered when heated with baryta water, but when boiled with concentrated hydrochloric acid, it decomposes into water and atropic acid.

(2) **Tropic Acid** is obtained by digesting the alkaloids, atropine and belladonna, with baryta water. It is formed artificially, by boiling β-chlorhydro-atropic acid (p. 759), with a solution of potassium carbonate (*Annalen*, 209, 25). The acid dissolves with more difficulty in water; crystallizes in needles or plates, and melts at 117°. It is inactive, but can be resolved into a *lævo-* and *dextro*-form by the crystallization of its quinine salt. The dextro-variety crystallizes in bright vitreous prisms and leaflets; it melts at 128°. The lævo-form melts about 123° (*Berichte*, 22, 2590). It decomposes into water and atropic acid when boiled with baryta water.

(3) **β-Phenyl-lactic Acid**, $C_6H_5.CH_2.CH.(OH).CO_2H$, Benzyl-glycollic acid, is derived from phenylacetaldehyde (p. 721), with prussic acid and hydrochloric acid, and from benzyl-tartronic acid upon heating it to 180°. The acid crystallizes from water in large prisms, melts at 97°, and when heated to 130° with dilute sulphuric acid decomposes into phenylacetaldehyde and formic acid. Boiling water does not alter it.

(4) **β-Phenyl-hydracrylic Acid**, $C_6H_5.CH(OH).CH_2.CO_2H$, commonly called *phenyl-lactic acid*, results on boiling β-brom-hydro-cinnamic acid (p. 757) with water, or by the addition of hypochlorous acid to cinnamic acid:—

$$C_6H_5.CH{:}CH.CO_2H + ClOH = C_6H_5.CH(OH).CHCl.CO_2H,$$

and then reducing the resulting chlor-acid with sodium amalgam. The acid is very soluble in cold water, and melts at 94°. When heated with dilute sulphuric acid it decomposes (like the β-oxy-acids) at 100° into water and cinnamic acid (together with a little styrolene) (*Berichte*, 13, 304). When digested with the haloid acids it forms phenyl-β-haloid-propionic acids (p. 758).

Phenyl-halogen-lactic acids (p. 359):—

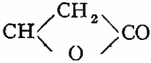
$$\underset{\text{Phenyl-}\alpha\text{-chlorlactic acid.}}{C_6H_5.CH(OH).CHCl.CO_2H} \text{ and } \underset{\text{Phenyl-}\beta\text{-brom-lactic acid.}}{C_6H_5.CHBr.CH(OH).CO_2H.}$$

The first of these is produced by the action of chlorine in alkaline solution upon phenyl-acrylic acid (cinnamic acid) (see above, and also *Annalen*, 219, 184). It crystallizes with one molecule of water, which escapes in the dessicator. When it contains water it melts at 79°, when anhydrous at 104°. **Phenyl-α-bromlactic Acid** is produced on boiling cinnamic dibromide (p. 757) with water. It crystallizes in leaflets, containing $1H_2O$, melts at 121°, loses water of crystallization, and then melts at 125°. When boiled with alkalies both acids yield phenylacetaldehyde (p. 721), together with β-phenylglyceric acid (see *Annalen*, 219, 180).

Phenyl-β-brom-lactic Acid (see above) is produced when hydrobromic acid acts upon β-phenylglyceric acid (p. 782). It has not been further described (*Berichte*, 16, 2820).

Nitro-phenyl-lactic Acids, $C_6H_4(NO_2).CH(OH).CH_2.CO_2H$.

The three isomerides (ortho, meta and para) are obtained from the three nitro-cinnamic acids by the addition of hydrogen bromide, and by the action of the alkalies, when their *β-lactones* (p. 353)—in the cold—are also produced, $C_6H_4(NO_2)$.



$CH{<}\begin{matrix}CH_2\\O\end{matrix}{>}CO$ (*Berichte*, 16, 2209, 17, 595).

The ortho nitro-acid results further by the condensation of *o*-nitro-benzaldehyde with acetaldehyde by means of a little bartya water, and by oxidizing the aldehyde first produced with silver oxide (*Berichte*, 16, 2206). It melts at 126°, and when heated to 190° with dilute sulphuric acid yields *o*-nitro-cinnamic acid. Its *β*-lactone melts at 124°, and decomposes on boiling with water into carbon dioxide and *o*-nitrostyrolene; it yields oxydihydrocarbostyril when reduced (*Berichte*, 17, 2011).

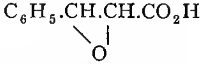
The meta-nitro-acid melts at 105°; its *β*-lactone at 98°. The para-nitro-acid, obtained by oxidizing *p*-nitro-cinnamic aldehyde with argentic oxide, melts at 132°, and its lactone at 92°. When the three nitro acids are heated with alcoholic zinc chloride, we do not get their lactones, but their esters (*Berichte*, 17, 1659).

Two **phenyl-oxyacrylic acids, or oxy-cinnamic acids,** have been prepared by the action of alcoholic potash upon phenylchlor- and brom-lactic acids (*Berichte*, 16, 2815):—

$$C_6H_5.CH{:}C(OH).CO_2H \text{ and } C_6H_5.C(OH){:}CH.CO_2H.$$

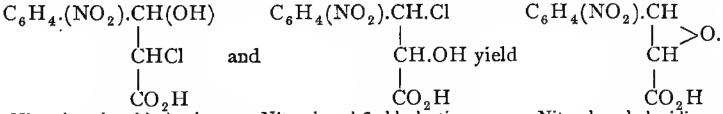
Phenyl-*α*-oxyacrylic Acid. Phenyl-*β*-oxyacrylic Acid.

One, at least, of these acids represents *Phenylglycidic acid*, $C_6H_5.CH.CH.CO_2H$ (*Berichte*, 20, 2465).



$$C_6H_5.\underbrace{CH.CH}_{O}.CO_2H$$

The **nitrophenyl-glycidic acids** (p. 456), obtained by saponifying the nitrophenylchlor-lactic acids with alcoholic potash, have been studied more fully:—



$$\begin{array}{c} C_6H_4.(NO_2).CH(OH) \\ | \\ CHCl \\ | \\ CO_2H \end{array} \text{ and } \begin{array}{c} C_6H_4(NO_2).CH.Cl \\ | \\ CH.OH \\ | \\ CO_2H \end{array} \text{ yield } \begin{array}{c} C_6H_4(NO_2).CH \\ | \quad >O. \\ CH \\ | \\ CO_2H \end{array}$$

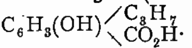
Nitrophenyl-*α*-chlorlactic Acid. Nitrophenyl-*β* chlorlactic Acid. Nitrophenyl-glycidic Acid.

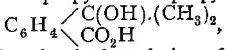
Para-nitrophenylglycidic acid melts at 280° with decomposition. It unites with hydrochloric acid to *p*-nitrophenyl-*β*-chlorlactic acid, which, like the *α*-acid, melts at 167–168°. Alcoholic potash again changes it to glycidic acid. Sulphuric acid and water convert glycidic acid into *p*-nitrophenyl-glyceric acid.

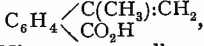
Ortho-nitrophenyl glycidic acid, from *o*-nitrocinnamic acid (*Berichte*, 13, 2262), contains one molecule of water and melts at 94°. When anhydrous, it melts at 108°. It combines with hydrochloric acid to *o*-nitrophenyl-*β*-chlorlactic acid, melting at 126°. Alcoholic potash regenerates glycidic acid (*Berichte*, 19, 2649). Anthranil and anthroxanaldehyde result when *o*-nitroglycidic acid is boiled with water.

Acids, $C_{10}H_{12}O_3$.

1. **Phenyl-*γ*-oxybutyric Acid,** $C_6H_5.CH(OH).CH_2.CH_2.CO_2H$, is precipitated in the cold, from its salts, by hydrochloric acid. It melts at 75°, with decomposition into water and its lactone—**phenyl-butyrolactone,** $C_{10}H_{10}O_2$. The latter is obtained from phenyl-brombutyric acid (from isophenylcrotonic acid) with a soda solution. It melts at 37°, and boils at 306° (*Annalen*, 216, 103).

2. **Propyloxybenzoic Acids,**  $C_6H_3(OH)\begin{cases} C_3H_7 \\ CO_2H \end{cases}$. Six of the twenty possible isomerides, having this formula (normal propyl and isopropyl), are known.

3. **Oxyisopropylbenzoic Acid,**  $C_6H_4\begin{cases} C(OH).(CH_3)_2 \\ CO_2H \end{cases}$, oxycumic acid, is obtained from cumic acid (p. 760), by the hydroxylation of the isopropyl group.

This is effected by the oxidation with potassium permanganate (p. 346). It crystallizes from hot water in thin prisms, and melts at 156°. Its sulpho-acid is similarly formed from paracymene and paraisocymene-sulphonic acid (p. 522) with potassium permanganate. When boiled with hydrochloric acid it parts with water, and becomes **Propenylbenzoic Acid,**  $C_6H_4\begin{cases}C(CH_3){:}CH_2\\CO_2H\end{cases}$, which melts at 161°. Similarly, nitrocumic acid yields **Nitro-oxypropylbenzoic Acid,** and **Nitropropenylbenzoic Acid,** and by the reduction of the latter, the *amido acids.* Amido-oxypropylbenzoic acid yields the *cumazonic* compounds (*Berichte,* 16, 2577, 17, 1303), which are analogous in constitution to the ethenyl-amido-phenols (p. 683). With nitrous acid amido-oxypropenyl benzoic acid affords methyl-cinnolinecarboxylic acid (*Berichte,* 17, 724).

MONOBASIC DIOXYACIDS.

1. *Dioxybenzoic Acids,* $C_7H_6O_4 = C_6H_3.(OH)_2.CO_2H$. These are also termed the carboxylic acids of the corresponding dioxybenzenes, $C_6H_4(OH)_2$ (Resorcinol, pyrocatechin, hydroquinone), since they can be obtained from the latter by the direct introduction of carboxyl (on heating with ammonium carbonate or potassium carbonate, p. 767), or by the oxidation of the corresponding aldehydes, $C_6H_3(OH)_2.CHO$ (p. 723). Three of the six possible isomerides are derived from resorcinol (1, 3), two from pyrocatechin (1, 2), and one from hydroquinone (1, 4). Conversely, by the elimination of carbon dioxide from the acids we regenerate the dioxybenzenes.

(1) Symmetrical *Dioxbenzoic Acid* (1, 3, 5), α-resorcylic acid, corresponding to orcinol, is obtained from α-disulphobenzoic acid (p. 692) on fusion with potassium hydroxide. It crystallizes with 1½H_2O, melts at 233°, and by the exit of carbon dioxide yields resorcinol. Ferric chloride does not color it. When distilled or heated with sulphuric acid to 130° it yields anthrachrysone, a derivative of anthracene. Its *dimethyl ether,* $C_6H_3(O.CH_3)_2.CO_2H$, is produced on oxidizing dimethylorcin, and melts at 176°.

(2) **β-Resorcylic Acid** (1, 2, 4 — CO_2H in 1) is obtained on heating resorcinol with potassium carbonate (*Berichte,* 18, 1985), also on fusing β-disulphobenzoic acid and β-resorcylaldehyde (also umbelliferon) with caustic potash. It dissolves with difficulty in cold water, crystallizes with 1½, 2½ and 3 molecules of water in fine needles, melting in the anhydrous state at 213°, and decomposing into CO_2 and resorcin. Ferric chloride colors it a dark red. *Peonol* is a derivative of β-resorcylic acid (*Berichte,* 19, 1777).

(3) **γ-Resorcylic Acid** (1, 2, 6 — CO_2H in 1) is formed together with β-resorcylic acid from resorcinol, by means of ammonium carbonate (*Berichte,* 13, 2380); it decomposes about 150° into CO_2 and resorcinol, and is colored a blue-violet by ferric chloride. On warming it reduces alkaline copper and silver solutions.

(4) **Hydroquinone Carboxylic Acid** (1, 4, CO_2H), *Oxysalicylic Acid,* was first prepared from gentisin, hence called *gentisinic acid.* It is obtained from brom-, *p*-iodo-, and amido-salicylic acids; also from hydroquinone by means of a potassium dicarbonate solution, and by fusing gentisinic aldehyde (from hydroquinone with potassium hydroxide (*Berichte,* 14, 1988). It melts at 200°, and at

215° breaks up into carbon dioxide and hydroquinone. Ferric chloride colors it a deep blue. On warming it reduces alkaline copper and ammoniacal silver solutions. When oxidized it yields a yellow-colored acid, which is decolorized by reducing agents, and is in all probability quinone carboxylic acid, $C_6H_3(O_2).CO_2H$.

(5) **Pyrocatechin-ortho-carboxylic Acid** (1, 2, 3 — CO_2 in 1) is obtained from *m*-iodo-salicylic acid by fusion with KOH, and from pyrocatechin on heating with ammonium carbonate to 140° (together with protocatechuic acid). It crystallizes in small needles (with $2H_2O$), is colored an intense blue by ferric chloride, melts at 204°, and decomposes further into carbon dioxide and pyrocatechin (*Annalen*, 220, 117).

(6) **Protocatechuic Acid,** $C_6H_3\left\{\begin{matrix}(OH)_2\\ CO_2H\end{matrix}\right.$ (1, 3, 4 — CO_2H in 1), Pyrocatechin-para-carboxylic acid, is obtained from many benzene tri-derivatives (*e.g.*, brom- and iodo-para-oxybenzoic acids, bromanisic acid, para- and meta-cresolsulphonic acid, eugenol, catechin), as well as from various resins (benzoïn, asafœtida, myrrh) on fusion with potassium hydroxide (and usually together with some paraoxybenzoic acid); furthermore, on heating hydroquinone with ammonium carbonate (together with pyrocatechin ortho-carboxylic acid) and by the action of bromine upon quinic acid. It is most easily prepared from kino by adding the latter to fused caustic soda (*Annalen*, 177, 188). It crystallizes with one molecule of water in shining needles or leaflets, and dissolves readily in hot water, alcohol and ether. At 100° it loses its water of crystallization, melts at 199°, and decomposes further into carbon dioxide and pyrocatechin. Ferric chloride colors the solution green; after the addition of a very dilute soda solution it becomes blue, later red (all derivatives containing the protocatechuic residue, $(OH)_2C$— *Berichte*, 14, 958, react similarly). Ferrous salts color its salt solutions violet. It reduces an ammoniacal silver solution, but not an alkaline copper solution.

Diprotocatechuic Acid, $C_{14}H_{10}O_7$, is a tannic acid, which results on boiling the preceding with aqueous arsenic acid. It is very similar to common tannic acid, but is colored green by ferric oxide.

The dimethyl- and diethyl-protocatechuic acids are obtained by heating with potassium hydroxide and methyl or ethyl iodide.

Dimethyl-protocatechuic Acid, $C_6H_3\left\{\begin{matrix}(O.CH_3)_2\\ CO_2H\end{matrix}\right.$, also results from dimethyl-protocatechuic aldehyde (p. 726), methyl creosol (p. 693) and methyl eugenol, on oxidation with potassium permanganate. It is the so-called *veratric acid*, $C_9H_{10}O_4$, which occurs together with *veratrin* (see the alkaloids) in the sabadilla seeds (from *Veratrum Sabadilla*). It crystallizes from hot water in needles, melting at 179.5°. Heated to 150° with hydrochloric acid, it splits off a methyl group and yields the two monomethyl compounds. When digested with lime or baryta it decomposes into carbon dioxide and dimethyl-pyrocatechin (p. 690).

Diethylprotocatechuic acid melts at 149°.

Monomethyl-protocatechuic Acids, $C_8H_8O_4$:—

$$(1)\ C_6H_3\left\{\begin{array}{ll}CO_2H & (1)\\ O.CH_3 & (3)\\ OH & (4)\end{array}\right. \quad\text{and}\quad (2)\ C_6H_3\left\{\begin{array}{ll}CO_2H & (1)\\ OH & (3).\\ O.CH_3 & (4)\end{array}\right.$$

The first body is **vanillic acid**, obtained by the energetic oxidation of its aldehyde, vanillin (and from coniferine, p. 725), also from aceteugenol, acetferulic acid, and from aceto-homovanillic acid when oxidized with potassium permanganate (p. 781). It crystallizes from hot water in shining needles, melts at 211°, and can be sublimed. When it is heated to 150° with hydrochloric acid it decomposes into methyl chloride and protocatechuic acid; distilled with lime it yields guaiacol. When methylated it is converted into dimethyl-protocatechuic acid, from which it is again regained by a partial demethylation.

Isomeric monomethyl-protocatechuic acid (Formula 2),—**Isovanillic Acid**,—was first obtained from hemipinic acid, and is prepared together with vanillic acid by methylating protocatechuic acid, or by demethylating dimethyl-protocatechuic acid, and by oxidizing hesperitinic acid. It melts at 250°.

Coniferyl alcohol (p. 725), eugenol and ferulic acid, stand in close relation to vanillic acid; they contain unsaturated side-chains, and, therefore, are treated in connection with the cinnamic acid derivatives. Meconine, opianic acid and hemipinic acid bear close genetic relation.

The methylene ether of protocatechuic acid is

Piperonylic Acid, $C_8H_6O_4 = C_6H_3\left(\begin{matrix}O\\O\end{matrix}\!>CH_2\right).CO_2H$, Methylene-proto-catechuic acid, which is formed upon oxidizing its aldehyde, piperonal (p. 725), and safrol with potassium permanganate. It is prepared synthetically by heating protocatechuic acid with methylene iodide and potassium hydroxide, and can be decomposed conversely into protocatechuic acid and carbon on heating with hydrochloric acid. It sublimes in fine needles, melting at 228°, and is soluble with difficulty in hot water. Heated to 210° with water it breaks up into pyrocatechin, carbon dioxide and carbon.

Ethylene-protocatechuic acid is a perfect analogue of piperonylic acid. It is prepared by means of ethylene bromide, and melts at 133°.

Ether derivatives of protocatechuic acid and the trivalent phenol, phloroglucin (p. 695), are:—**Luteolin**, **Maclurin**, and **Catechin**. The first, $C_{20}H_{12}O_8$, occurs in *Reseda luteola* and crystallizes in yellow needles. Ferric chloride colors it green. When fused with potassium hydroxide it is resolved into protocatechuic acid and phloroglucin:—

$$C_{20}H_{12}O_8 + 3H_2O = 2C_7H_6O_4 + C_6H_3(OH)_3.$$

The second and third bodies are generally included among the tannic acids. They also are decomposed into protocatechuic acid and phloroglucin on fusion with potassium hydroxide.

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2. *Acids*, $C_8H_8O_4$.

(*a*) Dioxyphenyl-acetic Acids, $C_6H_3(OH)_2.CH_2.CO_2H$.

1. **Homoprotocatechuic Acid** and **Homovanillic Acid**, its monomethyl ether, have their side-groups occupying the same positions as those of protocatechuic and vanillinic acids:—

$$C_6H_3\left\{\begin{array}{ll}CH_2.CO_2H & (1)\\ OH & (3)\\ OH & (4)\end{array}\right. \quad\text{and}\quad C_6H_3\left\{\begin{array}{ll}CH_2.CO_2H & (1)\\ O.CH_3 & (3).\\ OH & (4)\end{array}\right.$$

The latter is produced, along with vanillic acid, by the careful oxidation of aceteugenol, $C_6H_3(C_3H_5)\begin{cases} O.CH_3 \\ O.C_2H_3O \end{cases}$, and the saponification of the acetyl derivative produced at first. It melts at 143°, and when heated with hydrochloric acid to 180° yields homo-protocatechuic acid, melting at 127°, and methyl chloride. Homopyrocatechin is produced when it is heated with lime.

2. **Symmetrical Dioxyphenyl-acetic Acid** (1, 3, 5).

The triethyl ester, obtained from the dicarboxylic acid derived from this acid, is produced by the condensation of acetone dicarboxylic ester (p. 566). It melts at 98° and yields dioxyphenyl-acetic acid upon saponification (two molecules of carbon dioxide are eliminated at the same time). The acid is soluble in water, alcohol and ether. It crystallizes with one molecule of water and melts at 54°. It resembles orcin in its reactions, and yields the latter when its silver salt is heated (*Berichte*, 19, 1449).

(*b*) Dioxytoluic Acids, $C_6H_2(OH)_2\begin{cases} CH_3 \\ CO_2H \end{cases}$.

There are five isomerides. Of these orsellic or lecanoric acid, $C_{16}H_{14}O_7 + H_2O$, is found in different mosses of the varieties Roccella and Lecanora. It can be extracted from the same by means of ether or milk of lime. Its crystals are almost perfectly insoluble in water, melt at 153°, and are colored red by ferric chloride. Boiling with lime changes it to *orsellinic acid*, $C_8H_8O_4$. The latter consists of easily soluble prisms, and is colored violet by ferric chloride. It melts at 176°, and decomposes into carbon dioxide and orcin, $C_6H_3(CH_3)(OH)_2$ (p. 692).

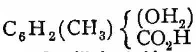
Erythrin, $C_{20}H_{22}O_{10}$ (Erythrinic Acid), is an ether-like derivative of orsellinic acid and erythrite, $C_4H_6(OH)_4$ (p. 474). It occurs in the lichen *Roccella fusciformis*, which is applied in the manufacture of archil (p. 693) and is extracted from it by means of milk of lime. Erythrin crystallizes with 1½ molecules of H_2O and is soluble with difficultly in hot water. Exposure to the air causes it to assume a red color. When it is boiled with water or baryta-water it breaks up into orsellinic acid and picroerythrin:—

$$C_{20}H_{22}O_{10} + H_2O = C_8H_8O_4 + C_{12}H_{16}O_7.$$

Picro-erythrin, $C_{12}H_{16}O_7 + H_2O$, forms crystals, which dissolve readily in alcohol and ether, and on further boiling with baryta water yield erythrite, orcin and carbon dioxide:—

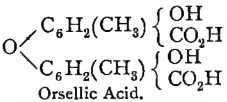
$$C_{12}H_{16}O_7 + H_2O = C_4H_{10}O_4 + C_7H_8O_2 + CO_2.$$

The structure of the preceding compounds is as follows:—

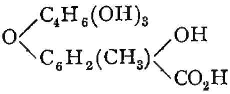


$$C_6H_2(CH_3)\begin{cases} (OH_2) \\ CO_2H \end{cases}$$

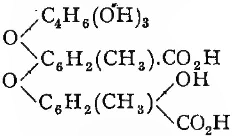
Orsellinic Acid.



Orsellic Acid.
Diorsellinic Acid.



Picroerythrin.
Erythro-orsellinic Ether.

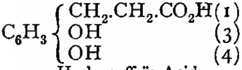


Erythrin.
Erythro-diorsellinic Ether.

3. *Acids*, $C_9H_{10}O_4$.

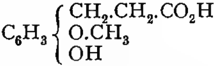
Hydro-umbellic Acid, $C_6H_3(OH)_2.CH_2.CH_2.CO_2H$ (1, 2, 4 — CH_2 in 1). The position of its side-chains is the same as in β-resorcylic acid (p. 778). It is obtained from umbellic acid, $C_9H_8O_4$, and umbelliferon, $C_9H_6O_3$ (see this), by the action of sodium amalgam. Above 110° it decomposes, water separating, and melts at 120°. Ferric chloride colors it green. It reduces alkaline copper and silver solutions. It yields resorcinol on fusion with KOH.

Hydrocaffeïc Acid, $C_9H_{10}O_4$.



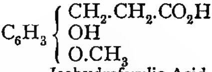
$$C_6H_3\left\{\begin{array}{ll}CH_2.CH_2.CO_2H & (1)\\ OH & (3)\\ OH & (4)\end{array}\right.$$

Hydrocaffeïc Acid.



$$C_6H_3\left\{\begin{array}{l}CH_2.CH_2.CO_2H\\ O.CH_3\\ OH\end{array}\right.$$

Hydroferulic Acid.



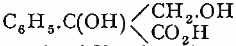
$$C_6H_3\left\{\begin{array}{l}CH_2.CH_2.CO_2H\\ OH\\ O.CH_3\end{array}\right.$$

Isohydroferulic Acid.

The hydrocaffeïc acid, with the same arrangement of side-chains as in protocatechuic acid, is obtained from caffeïc acid by the action of sodium amalgam; is colored the same by ferric chloride, etc., as the protocatechuic acid (779), and reduces both alkaline copper and silver solutions. **Hydroferulic** and **Isohydroferulic Acids** are its monomethyl ethers. They correspond to vanillic and isovanillic acids. Sodium amalgam converts ferulic and isoferulic acids into the above hydro-acids. The former melts at 90°, the latter at 147°.

Everninic Acid, $C_9H_{10}O_4$, is produced, together with orsellinic acid, on boiling *evernic acid*, $C_{17}H_{16}O_7$ (from *Evernia Prunastri*), with baryta. It melts at 157°, and is colored violet by ferric chloride.

Dioxy-alcoholic Acids, $C_9H_{10}O_4$.



$$C_6H_5.C(OH)\begin{array}{l}\diagup CH_2.OH\\ \diagdown CO_2H\end{array}$$

α-Phenyl Glyceric Acid.

$C_6H_5.CH(OH).CH(OH).CO_2H.$

β-Phenyl Glyceric Acid.

The **α-Acid** (**Atroglyceric Acid**) results on boiling dibrom-hydro-atropic acid (p. 759) with excess of alkalies, and from benzoyl carbinol (p. 712) by means of prussic acid and hydrochloric acid (*Berichte*, 16, 1292). It crystallizes from water in warty masses, and melts at 146°.

The **β-Acid** (**Phenylstyceric Acid**) is obtained from αβ-dibromhydrocinnamic ester (p. 757) by first getting the dibenzoyl ester and saponifying it, or by boiling phenyl-α-chlorlactic acid and the two phenyloxyacrylic acids (p. 777) with water (together with phenylacetaldehyde); also by oxidizing cinnamic acid, $C_6H_5.CH:CH.CO_2H$, with potassium permanganate (p. 460) (*Berichte*, 21, 920). It is a crystalline mass, very soluble in water, and melts at 143°, with decomposition into phenylacetaldehyde, carbon dioxide and water. *p-* and *o-Nitro-phenyl glyceric acids* have been obtained from nitrophenyl-glycidic acids (p. 777).

MONOBASIC TRIOXYACIDS.

Trioxybenzoic Acids, $C_7H_6O_5$. Three of the six possible isomerides are known :—

1. **Gallic Acid**, $C_6H_2(OH)_3.CO_2H$ (1, 3, 4, 5—CO_2H in 1), occurs free in gall nuts, in tea, in the fruit of *Cæsalpinia coriaria* (Divi-divi), in mangoes, and in various other plants. When combined, and then chiefly as a glucoside, it occurs in some tannic

acids. It is obtained from the ordinary tannic acid (tannin) by boiling it with dilute acids. It is prepared artificially on heating di-iodo-salicylic acid to 130° with potassium carbonate, and from brom-dioxy-benzoic acid, brom-proto-catechuic and veratric acids (p. 779) when fused with potassium hydroxide.

Gallic acid arises, like pyrogallol carboxylic acid (below), from the *adjacent* trioxybenzene (pyrogallol). Since the carboxyl in the latter occupies the ortho-position referred to a hydroxyl, and since but 2 pyrogallol acids are possible, gallic acid would then be the second isomeride (*Berichte*, 17, 1090).

Gallic acid crystallizes in fine, silky needles, containing one molecule of water. It dissolves in three parts of boiling, and 130 parts of water at 12°, and readily in alcohol and ether. It has a faintly acid, astringent taste. It melts and decomposes near 220°, into carbon dioxide, and pyrogallol, $C_6H_3(OH)_3$. It reduces both gold and silver salts (hence its application in photography). Ferric chloride throws down a blackish-blue precipitate in its solutions.

Although gallic acid is monobasic, it can, by virtue of its being a trivalent phenol, combine also to salts with four equivalents of metal. The solutions of the alkali salts absorb oxygen when exposed to the air, and, in consequence, become brown in color.

Gallic acid forms a *triacetate*, $C_6H_2(O.C_2H_3O)_3.CO_2H$, with acetyl chloride. This crystallizes from alcohol in needles. The *ethyl ester*, $C_6H_2(OH)_3.CO_2.C_2H_5$. crystallizes with 2½ molecules of H_2O and is soluble in water. When anhydrous it melts at 150°, and sublimes. *Triethyl-gallate*, $C_6H_2(O.C_2H_5)_3.CO_2H$, from gallic acid, melts at 112°, and forms an easily soluble barium salt.

Rufigallic Acid, $C_{14}H_8O_8$, a derivative of anthracene (see this) is obtained by heating gallic acid with four parts of sulphuric acid to 140°.

Oxidizing agents, such as arsenic acid, silver oxide, iodine and water, convert gallic into *Ellagic Acid*, $C_{14}H_8O_9$. The latter occurs in the bezoar stones (an intestinal calculus of the Persian goat). It is obtained from this source by boiling with potassium hydroxide, and precipitating with hydrochloric acid. Ellagic acid separates out in the form of a powder containing 1 molecule of water of crystallization. It is insoluble in water.

2. **Pyrogallol-carboxylic Acid**, $C_6H_2(OH)_3CO_2H$ (1, 2, 3, 4—CO_2 in 1), is isomeric with gallic acid, and is prepared by heating pyrogallol with ammonium carbonate. It dissolves with more difficulty in water, crystallizes in shining needles containing ⅓H_2O, and sublimes without decomposition in a current of carbon dioxide. Ferric chloride colors it violet and greenish-brown; it also reduces alkaline copper and silver solutions. *Triethyl-pyrogallol-carboxylic Acid*, $C_6H_2(O.C_2H_5)_3.CO_2H$, crystallizes in long shining needles, and melts at 105°. It also results in the oxidation of triethyldaphnetic acid (vide this). It yields triethyl pyrogallol by the elimination of carbon dioxide (p. 695).

3. **Phloroglucin Carboxylic Acid**, $C_6H_2(OH)_3.CO_2H$ (1, 2, 4, 6—CO_2H in 1), may be obtained by heating phloroglucin with potassium bicarbonate. It crystallizes with one molecule of water, is very unstable and decomposes even at 100°, also when boiled with water, into carbon dioxide and phloroglucin.

4. **Oxy-hydroquinone Carboxylic Acid**, $C_6H_2(OH)_3.CO_2H$(1, 2, 4, CO_2H), is not known in a free condition. Its triethyl-ether acid, $C_6H_2(O.C_2H_5)_3.CO_2H$, has been obtained from æsculetin. It melts at 134°, splits off carbon dioxide and becomes triethyl-oxyhydroquinone (p. 696).

TANNIC ACIDS.

The tannins or tannic acids are substances widely disseminated in the vegetable kingdom. They are soluble in water, possess an acid, astringent taste, are colored dark blue or green (ink) by ferric salts, precipitate gelatine and enter into combination (leather) with animal hides (gelatine). Hence they are employed in the manufacture of leather, and for the preparation of ink. They are precipitated from their aqueous solutions by neutral acetate of lead.

Some tannic acids appear to be glucosides of gallic acid, *i. e.*, ethereal compounds of the same with various sugars. They decompose into gallic acid and grape sugar upon boiling with dilute acids. Others contain phloroglucin, $C_6H_3(OH)_3$, instead of grape sugar. Common tannic acid, tannin, appears to be, at least in a pure state, not a glucoside but a digallic acid.

When the tannic acids are fused with potassium hydroxide they yield mostly protocatechuic acid and phloroglucin.

Tannic Acid, Tannin, $C_{14}H_{10}O_9 + 2H_2O$, **Digallic Acid,** occurs in large quantity (upwards of 50 per cent.), in gall nuts (pathological concretions upon the different oak species, *Quercus infectoria*, produced by the sting of insects); in sumach (*Rhus coriaria*), in tea and in other plants. It is prepared artificially by oxidizing gallic acid with silver nitrate, by heating it with phosphorus oxychloride to 130°, or by boiling with dilute arsenic acid. Conversely, it passes, on boiling with dilute acids or alkalies, into gallic acid (without the appearance of sugar):—

$$C_{14}H_{10}O_9 + H_2O = 2C_7H_6O_5.$$

Pure tannin must, therefore, be considered a digallic acid (*Berichte*, 17, 1478).

Tannin is best obtained from gall-nuts. The latter are finely divided and extracted with ether and alcohol. The solution separates into two layers, the lower of which is aqueous and contains tannin chiefly, and this is obtained by evaporation.

Pure tannic acid is a colorless, shining, amorphous mass, very soluble in water, slightly in alcohol, and almost insoluble in ether. Many salts (*e. g.*, sodium chloride) precipitate it from its aqueous solutions, and it can also be removed from the latter with ether. It reacts acid and is colored dark-blue by ferric chloride; gelatine precipitates it. Quantitative methods of estimating tannin are based on this behavior.

The acid generally forms salts with two equivalents of metal; these are obtained pure with difficulty. Acetic anhydride converts the acid into a *penta-acetate*,

$C_{14}O_5(C_2H_3O)_5O_9$. Heated to 210° it decomposes with formation of pyrogallol, $C_6H_3(OH)_3$.

Gallyl-gallic Acid, $C_{14}H_{10}O_9$, a keto-tannic acid, forms an oxime and phenylhydrazone, see *Berichte*, **22**, Ref. 754; **23**, Ref. 24.

The other tannic acids found in plants have been but little investigated: we may mention:—

Kino-tannin, which constitutes the chief ingredient of kino, the dried juice of *Pterocarpus erinaceus* and *Coccoloba uvifera*. Its solution is colored green by ferric salts. It yields phloroglucin on fusion with potassium hydroxide.

Catechu-Tannin occurs in catechin, the extract of *Mimosa Catechu*. Ferric salts color it a dirty-green (p. 779). *Catechin* or *Caterhinic Acid*, $C_{21}H_{20}O_9 + 5H_2O$, is also present in catechu. It crystallizes in shining needles.

Moringa-Tannin, $C_{13}H_{10}O_6 + H_2O$, *Maclurin*, is found in yellow wood (*Morus tinctoria*) from which it may be extracted (along with morin) with hot water. When the solution cools morin separates out; maclurin is precipitated from the concentrated liquid by hydrochloric acid, in the form of a yellow crystalline powder, soluble in water and alcohol. Ferric salts impart a greenish-black color to its solutions. When fused with caustic potash it yields protocatechuic acid and phloroglucin.

Morin, $C_{13}H_8O_6 + 2H_2O$, decomposes into phloroglucin and resorcin. Nitric acid oxidizes it to β-resorcylic acid.

The *Tannin* of *Coffee*, $C_{30}H_{18}O_{16}$, occurs in coffee beans and Paraguay tea. Gelatine does not precipitate its solutions. Ferric chloride gives them a green color. It decomposes into caffeïc acid (see this) and sugar, when boiled with potassium hydroxide. Protocatechuic acid is produced when it is fused with potassium hydroxide.

The *Tannin* of *Oak* is found in the bark (together with gallic acid, ellagic acid, quercite). It has the formula $C_{19}H_{16}O_{10}$, and is a red powder, not very soluble in cold water, but more readily in acetic ether. Ferric chloride colors its solution dark blue. Boiling, dilute sulphuric acid converts it into the so-called *oak-red* (phlobaphene), $C_{38}H_{26}O_{17}$.

The *Tannin* found in the quinine barks is combined with the quinia-alkaloids. It closely resembles ordinary tannic acid, but is colored green by ferric salts. When boiled with dilute acids it breaks up into sugar and *quina-red*, an amorphous brown substance, yielding protocatechuic acid and acetic acid on fusion with potassium hydroxide.

Quinic Acid is very probably derived from hexahydrobenzene, $C_6H_6(H_6)$ (p. 567), and must be considered tetraoxyhexahydrobenzene carboxylic acid, $C_6H(H_6)(OH)_4.CO_2H$. It is a polyhydric phenol carboxylic acid. It is converted into normal benzene derivatives in various reactions. Quercite is intimately related to it (p. 697).

Quinic Acid, $C_7H_{12}O_6$, is present in the cinchona barks, in coffee beans, in bilberry and many other plants. It is obtained as a secondary product in the preparation of quinine, by extracting the quinia bark with dilute sulphuric acid, and precipitating the alkaloids with milk of lime. When the filtered solution is evaporated the calcium salt of the acid separates out.

The acid consists of rhombic prisms, and dissolves very easily in water, but with difficulty in strong alcohol. The aqueous solution is lævo-rotatory. It melts at

162°, and upon further heating decomposes into hydroquinone, pyrocatechin, benzoic acid, phenol and other products. Oxidizing agents (MnO_2 and sulphuric acid) convert it into formic acid, carbon dioxide and quinone. Ferments decompose it into propionic acid, acetic acid and formic acid. It is a monobasic acid and furnishes easily soluble salts. The *calcium salt*, $(C_7H_{11}O_6)_2Ca + 10H_2O$, crystallizes in rhombic leaflets, which effloresce on exposure to the air.

Quinic acid is reduced by hydriodic acid to benzoic acid:—

$$C_6H_7(OH)_4.CO_2H + 2HI = C_6H_5.CO_2H + 4H_2O + I_2.$$

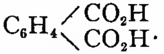
Phosphoric chloride converts it into chlor-benzoic chloride:—

$$C_6H_7(OH)_4.CO_2H + PCl_5 = C_6H_4Cl.COCl + PO_4H_3 + 3HCl + H_2O.$$

Acetic anhydride will convert its ethyl ester into tetracetyl-ethyl ester, $C_6H_7(O.C_2H_3O)_4CO_2.C_2H_5$, which yields large crystals, melting at 135°.

DIBASIC ACIDS.

Acids, $C_8H_6O_4$ =



$C_6H_4\begin{cases}CO_2H\\CO_2H\end{cases}$. There are three isomerides.

1. **Phthalic Acid,** $C_8H_6O_4$ is the ortho-dicarboxylic acid of benzene, and was first obtained by oxidizing naphthalene and chlorinated naphthalenes with nitric acid. It also results on oxidizing ortho-xylene and ortho-toluic acid with potassium permanganate, alizarin and purpurin with nitric acid, or with manganese dioxide and sulphuric acid; and in slight amount in the oxidation of benzene and benzoic acid. It is very difficult to get it by using chromic acid as an oxidizing agent, since the latter is very apt to burn it at once to carbon dioxide (p. 738). It can be synthetically obtained from *o*-nitrobenzoic acid by converting the latter into *o*-cyanbenzoic acid and then boiling this with alkalies (p. 752).

Preparation.—Boil naphthalene tetrachloride, $C_{10}H_8Cl_4$, with 10 parts of nitric acid (sp. gr. 1.45) until perfect solution is reached. Naphthalene tetrachloride is obtained by adding a mixture of naphthalene (2 parts) and potassium chlorate (1 part) to crude hydrochloric acid (11 parts) (*Berichte*, 11, 735).

Phthalic acid crystallizes in short prisms or in leaflets, which dissolve readily in hot water, alcohol and ether. It melts above 200°, decomposes at 140° into phthalic anhydride (melting at 128°) and water. When heated with an excess of calcium hydroxide it yields benzene and $2CO_2$. Only $1 CO_2$ is split off and calcium benzoate produced (p. 741) if its lime salt be heated to 330–350° with 1 molecule of $Ca(OH)_2$. Barium chloride added to aqueous ammonium phthalate precipitates barium phthalate, $C_8H_4O_4Ba$, which is very sparingly soluble in water.

PCl_5 converts phthalic acid, or phthalic anhydride at 170°, into phthalyl chloride, $C_6H_4(CO.Cl)_2$. In accord with all its transpositions this appears to have the constitution, $C_6H_4\left<\begin{matrix}CCl_2\\CO\end{matrix}\right>O$. Zinc and hydrochloric acid convert it into phthalide (p. 772), *diphthalyl*, $CO\left<\begin{matrix}C_6H_4\\O\end{matrix}\right>C : C\left<\begin{matrix}C_6H_4\\O\end{matrix}\right>CO$, and *hydrodiphthalyl* (*Berichte*, 21, Ref. 139), and with benzene and $AlCl_3$, or with mercury diphenyl it yields $C_6H_4\left<\begin{matrix}C(C_6H_5)_2\\CO\text{——}\end{matrix}\right>O$, phthalophenone, and with zinc ethyl,

Ethyl-phthalyl, $C_6H_4\left<\begin{matrix}C(C_2H_5)_2\\CO\text{——}\end{matrix}\right>O$, is produced. The latter does not combine with hydroxylamine (*Berichte*,17,817). Phenylhydrazine converts phthalyl chloride,or phthalic anhydride into phthalylphenylhydrazone,$C_6H_4\left<\begin{matrix}C(N_2H.C_6H_5)\\CO\text{——}\end{matrix}\right>O$, melting at 178° (*Berichte*, 19, Ref. 303; 20, Ref. 255). With hydroxylamine, phthalyl chloride yields the same *phthalyl-hydroxamic acid*, $C_6H_4\left<\begin{matrix}C(N.OH)\\CO\text{——}\end{matrix}\right>O$, melting at 230°, as is obtained from phthalic anhydride (*Berichte*, 16, 1781). Phthalyl chloride is a liquid boiling at 268°, and reverts to phthalic acid when boiled with water. The esters derived from phthalic chloride differ from those derived from phthalic acid (*Berichte*, 16,860). Sodium amalgam converts phthalyl chloride (unlike other transformations) into phthalyl alcohol (p. 712).

Phthalic Anhydride, $C_6H_4\left<\begin{matrix}CO\\CO\end{matrix}\right>O$ (see p. 402), is obtained by distilling phthalic acid or digesting it with acetyl chloride. It crystallizes in long, prismatic needles, melting at 128°, and boiling at 284°. It yields phthalyl-hydroxamic acid with hydroxylamine, and phthalylphenyl-hydrazone with phenylhydrazine. Zinc dust and glacial acetic acid convert it into phthalide (p. 772).

Phthalic anhydride readily condenses with unsaturated side-chains as a CO-group is present to take part in the reaction (p. 716). Thus, phthalyl acetic acid is formed on boiling the anhydride with acetic anhydride and sodium acetate, and ethine diphthalyl, $C_6H_4\left<\begin{matrix}C = CH - CH = C\\CO \quad\quad\quad\quad CO\end{matrix}\right>C_6H_4$ (with $>O$ and $O<$ between the groups) (*Berichte*, 18, 3115), when succinic anhydride and sodium acetate are used. It reacts in like manner with malonic ester and aceto-acetic ester (*Berichte*, 19, Ref. 832). It condenses with phthalide to diphthalyl (see this). Phthalic anhydride also condenses with the benzenes forming benzoylbenzoic acid and phenylphthalides. With the phenols it yields the important phthaleïn dyes (see these).

Phthalimide, $C_6H_4\left<\begin{matrix}CO\\CO\end{matrix}\right>NH$ or $C_6H_4\left<\begin{matrix}C(NH)\\CO\text{——}\end{matrix}\right>O$, is obtained:—

- By heating phthalic anhydride or chloride in ammonia gas, or by heating ammonium phthalate;
- By heating phthalic acid with ammonium or potassium sulphocyanide (p. 732) (*Berichte*, 19, 1398);
- By the molecular rearrangement of the isomeric *o*-cyanbenzoic acid (p. 752) (*Berichte*, 19, 2283).

Phthalimide crystallizes in six-sided prisms, which melt at 238°, and sublime. It forms *potassium phthalimide*, $C_6H_4(CO)_2NK$, by the action of alcoholic potash.

Salts of the heavy metals can be obtained from it by double decomposition. The metal in these salts can be replaced by various radicals (*Berichte*, 23, 994). Tin and hydrochloric acid reduce phthalimide to—

Phthalimidine,  $C_6H_4\left\langle\begin{matrix}C(NH)\\CH_2—\end{matrix}\right\rangle O$, which can also be made by a rearrangement of *o*-cyanbenzyl alcohol, $C_6H_4(CN).CH_2.OH$ (*Berichte*, 22, Ref. 9; 23, 2479).

Hydrophthalic Acids.

Phthalic acid can take up two, four and six hydrogen atoms, forming di-, tetra-, and hexahydrophthalic acids. These must be considered as derivatives of hexamethylene, and the partially reduced benzene nuclei, C_8H_{10} and C_6H_8. A. Baeyer's theory (*Annalen*, 258, 145; *Berichte*, 23, Ref. 577), based on the spatial configurations of van't Hoff as to the union of the C-atoms, is best explained by the scheme of Kekulè, and allows for seven dihydrophthalic acids (enantiomorphous forms not included): one geometrical and six structural isomerides. But one of the seven forms is known. It also supposes the existence of six tetrahydrophthalic acids (four structural isomerides and two geometrical isomerides—the four first are known), and two geometrically isomeric hexahydrophthalic acids. The latter isomerism is due to the different positions occupied by the carboxyls relatively to the plane of the hexamethylene ring, and corresponds to that of maleïc and fumaric acid (*Annalen*, 258, 176); hence the isomerides are termed *maleïnoid* and *fumaroid* (or *cis* and *trans*) forms. Baeyer indicates the structure of the di- and tetrahydro-acids by representing the double unions with Δ (see p. 568). The partially hydrided phthalic acids behave the same as the unsaturated acids of the paraffin series. They unite quite readily with bromine and are oxidized with ease by potassium permanganate.

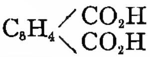
Dihydrophthalic Acid, $C_6H_4(H_2)(CO_2H)_2$ (1, 2), results from the action of sodium amalgam upon a cold solution of phthalic acid. The acid melts at 215°, combines readily with Br_2 and two molecules of hydrobromic acid, and is at once decomposed by potassium permanganate (*Berichte*, 23, Ref. 578).

Tetrahydrophthalic Acids, $C_6H_4(H_4)(CO_2H)_2$. Four of the six possible isomerides are known.

The Δ_1-*acid* is produced by the solution of its anhydride in hot water. It crystallizes in leaflets containing one molecule of water. They effloresce quite rapidly. The acid is very similar to pyrocinchonic acid (dimethyl maleïc acid, p. 430), and readily changes to its anhydride, $C_8H_8O_3$. The latter can also be obtained by the distillation of hydropyromellitic acid. It crystallizes from ether in leaflets. It melts at 74°, and is readily volatilized. Boiling potash converts the Δ_1-acid into the Δ_2-acid (*Berichte*, 23, Ref. 579; *Annalen*, 258, 161).

Δ_2- and Δ_4-Tetrahydrophthalic Acids are formed by reducing phthalic acid with sodium amalgam or by boiling dihydrophthalic acid. The first melts at 215–218°, and yields an anhydride, melting at 140°. The second acid yields the Δ_3-acid when heated to 220° or if boiled with water. The Δ_3-acid melts at 174°.

Hexahydrophthalic Acid, $C_6H_{10}(CO_2H)_2$, exists in a *fumaroid* and *maleïnoid* form. The first dissolves with difficulty and melts at 215°. It forms an anhydride with acetyl chloride, melting at 140°. The malëinoid form is more soluble in water and melts at 192°, forming an anhydride, melting at 32°. (For its analogy with fumaric and maleïc acids, see *Annalen*, 258, 176.)

2. **Isophthalic Acid**,  $C_6H_4\left\langle\begin{matrix}CO_2H\\CO_2H\end{matrix}\right.$ (1, 3), is obtained: by oxidizing isoxylene and isotoluic acid with a chromic acid mixture; by fusing potassium *m*-sulphobenzoate, *m*-brombenzoate and ben-

zoate with potassium formate (terephthalic acid is also formed in the last two cases); by the action of the ester of chlorcarbonic acid and sodium amalgam upon *m*-dibrombenzene; from *m*-dicyanbenzene (p. 735) and *m*-cyanbenzoic acid (p. 752); also by heating hydro-pyromellitic and hydro-prehnitic acid (p. 798), and by oxidizing colophony with nitric acid. Isophthalic acid crystallizes from hot water in fine, long needles. The most convenient method for its production consists in converting *m*-xylylene bromide into the diethyl ether and then oxidizing the latter (*Berichte*, **21**, 47). It is soluble in 460 parts boiling, and 7800 parts cold water. It melts above 300°, and sublimes in needles.

The *barium salt*, $C_8H_4O_4Ba + 3H_2O$, crystallizes in fine needles, and is very soluble in water; therefore, it is not precipitated by barium chloride from a solution of ammonium isophthalate (distinction between phthalic and terephthalic acids).

The *Dimethyl-isophthalate*, $C_6H_4(CO_2.CH_3)_2$, crystallizes from alcohol in needles, and melts at 65°. The *diethyl ester* is liquid, solidifies below 0°, and boils at 285°.

Isophthalyl Chloride, $C_8H_4O_2Cl_2$, is formed upon heating isophthalic acid with PCl_5 to 200°. Its formula is $C_6H_4(COCl)_2$. It melts at 41° and boils at 276°. There is only one tetrahydro-acid derived from the hydroisophthalic acids.

3. **Terephthalic Acid**, $C_6H_4(CO_2H)_2$ (1, 4), was first obtained by oxidizing turpentine oil. It results in oxidizing paraxylene, paratoluic acid and all di-derivatives of benzene having two carbon chains belonging to the para-series (*e. g.*, cymene and cumene) with chromic acid. The oxidation of crude xylene affords terephthalic (15 per cent.) and isophthalic (85 per cent.) acids, which are separated by means of their barium salts. Terephthalic acid is produced, too, when *p*-dicyanbenzene, $C_6H_4(CN)_2$ (p. 735), and *p*-cyanbenzoic acid are boiled with alkalies as well as from *p*-dibrombenzene, by the action of chlorcarbonic acid and sodium. The best course to pursue in forming terephthalic acid is to oxidize caraway oil (a mixture of cymene and cuminol) with chromic acid, or it may be prepared from *p*-toluidine by changing this into the nitrile, $C_6H_4(CH_3).CN$, etc. (*Berichte*, **22**, 2178).

Terephthalic acid is a powder, which is almost perfectly insoluble in water, alcohol and ether, and is, therefore, precipitated from its salts by acids. It sublimes without previous fusion when it is heated. Sometimes terephthalic acid is obtained with properties slightly different from the regular acid (insolic acid). The cause of this seems to be due to an admixture of acetophenone-carboxylic acid.

The *calcium salt*, $C_8H_4O_4Ca + 3H_2O$, and *barium salt*, $C_8H_4O_4Ba + 4H_2O$, are very sparingly soluble in water. The *methyl ester*, $C_8H_4(CH_3)_2O_4$, melts at 140°; the *ethyl ester*, at 44°.

Terephthalyl Chloride, $C_6H_4(COCl)_2$, is formed when terephthalic acid is heated with PCl_5. It melts at 78° and boils at 259°. It forms terephthalophenone with benzene and $AlCl_3$.

Nitroterephthalic Acid is produced when terephthalic acid is boiled with concentrated nitric acid. It melts at 259°. Reduction converts it into amidoterephthalic acid, $C_6H_3(NH_2).(CO_2H)_2$, which can be further changed to *cyanterephthalic Acid*, $C_6H_3(CN)(CO_2H)_2$ (*Berichte*, 19, 1634).

Hydroterephthalic Acids.

Ten hydroterephthalic acids are possible according to Baeyer's theory: five dihydro-, three tetra-hydro, and two hexahydro acids; three of these are geometrical isomerides (*Annalen*, 259, 1 and 149; *Berichte*, 23, Ref. 569, 577). The unsaturated hydrophthalic acids contain only double (no para) linkages. In deportment they are perfectly analogous to the unsaturated acids of the paraffin series, particularly muconic acid and the two hydro-muconic acids (*Berichte*, 23, Ref. 231). Ferricyanide of potassium oxidizes most of the hydro-acids to terephthalic acid. They are completely destroyed by potassium permanganate. With bromine the $\Delta_{1,\,3}$- and $\Delta_{1,\,5}$-dihydro-acids yield only dibromides, whereas the acids $\Delta_{1,\,4}$- and $\Delta_{2,\,5}$- yield tetrabromides. The first product in the oxidation of terephthalic acid is $\Delta_{2,\,5}$-dihydro-terephthalic acid. A *para* addition very probably occurs in this instance, which finds explanation, according to Baeyer, in the analogous deportment of muconic acid (*Annalen*, 208, 148; 256, 1).

The ten isomerides have all been prepared and differ in their constitution (Baeyer, *Berichte*, 23, Ref. 570).

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2. *Acids*, $C_9H_8O_4$. (1) Methylphthalic Acids, $C_6H_3(CH_3)\begin{cases}CO_2H\\CO_2H\end{cases}$.

Uvitic Acid, Mesidic Acid (1, 3, 5), is obtained by oxidizing mesitylene, $C_6H_3(CH_3)_3$, with dilute nitric acid (mesitylenic acid is produced at the same time, p. 756). It is formed synthetically by boiling pyroracemic acid with baryta water (p. 566). It crystallizes from hot water in needles, melting at 287°. Chromic acid oxidizes it to trimesic acid (p. 797); distilled with lime it at first yields metatoluic acid, then toluene (p. 741).

The synthesis of uvitic acid from pyroracemic acid is due to the *condensation* of three molecules of pyroracemic acid, with one molecule of acetaldehyde. In this reaction a portion of the pyroracemic acid is decomposed. If a mixture of pyroracemic acid and higher fatty aldehydes be used *homologous alkylisophthalic acids*, $C_6H_3(R)(CO_2H)_2$, will result. Thus propyl aldehyde produces ethylisophthalic acid, $C_6H_3(C_2H_5)(CO_2H)_2$, isobutyric aldehyde yields isopropyl isophthalic acid, etc. (Doebner, *Berichte*, 23, 2377).

Xylidic Acid, $C_6H_3(CH_3).(CO_2H)_2$, is obtained by oxidizing pseudocumene, $C_6H_3(CH_3)_3$ (1, 3, 4), xylic acid and so-called paraxylic acid with dilute nitric acid; hence its structure is (1, 3, 4—CH_3 in 3) (p. 756). Potassium permanganate oxidizes it to trimellitic acid. It separates from boiling water in flocculent masses; melts at 282° and sublimes.

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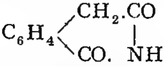
(2) Homophthalic Acids, $C_6H_4{<}{CH_2.CO_2H \atop CO_2H}$.

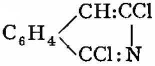
Phenylaceto-carboxylic Acid, Isouvitic Acid, is the ortho-compound. It may be obtained by fusing gamboge with caustic potash (*Berichte*, 19, 1654), and by saponifying cyan-*o*-toluic acid (from phthalide and potassium cyanide, p. 772). It crystallizes from hot water in stout prisms, melting at 175°, with the elimination of water. Its anhydride, $C_9H_6O_3$, obtained by digesting the acid with acetyl chloride, melts at 141°.

Homophthalimide, $C_9H_7NO_2$, is produced when the ammonium salt is heated. It crystallizes in minute needles, melting at 233° and distilling without decomposition. When it is heated with phosphorus oxychloride it yields dichlorisoquinoline, $C_9H_5NCl_2$, which becomes isoquinoline when further heated with hydriodic acid (*Berichte*, 19, 2354):—



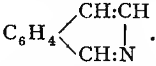
$C_6H_4\left\langle\begin{array}{l}CH_2.CO\\ \quad\ \ |\\ CO.\ NH\end{array}\right.$

Homophthalimide.



$C_6H_4\left\langle\begin{array}{l}CH{:}CCl\\ \quad\ \ |\\ CCl{:}N\end{array}\right.$

Dichlorisoquinoline.



$C_6H_4\left\langle\begin{array}{l}CH{:}CH\\ \quad\ \ |\\ CH{:}N\end{array}\right.$.

Isoquinoline.

Homophthalimide is directly converted into isoquinoline when it is heated with zinc dust; the reaction is analogous to the production of pyrrol from succinimide (*Berichte*, 21, 2299).

The hydrogen atoms of the CH_2-groups are replaced by two alkyls when homophthalimide is heated with caustic potash and alkyl iodides. *Mono*-alkyl derivatives of homophthalimide are also produced when *o*-cyanbenzyl cyanide, $C_6H_4\left\langle\begin{array}{l}CH_2.CN\\ CN\end{array}\right.$ (homophthalonitrile), is alkylized and further re-arranged (*Berichte*, 20, 2499).

The *para*-compound, *homoterephthalic acid*, $C_6H_4(CO_2H).CH_2.CO_2H$, has been obtained from *p*-cyanbenzyl cyanide, $C_6H_4.(CN).CH_2.CN$, and melts at 228° (*Berichte*, 22, 3216).

(3) **Phenyl Malonic Acid**, $C_6H_5.CH(CO_2H)_2$. The *ethyl ester of dinitrophenylmalonic acid* may be obtained from sodium malonic ester and bromdinitrobenzene. It forms yellow prisms, melting at 51°. It dissolves in the alkalies forming dark-red colored salts (*Berichte*, 21, 2740). *Dinitrobromphenylmalonic ester* (*Berichte*, 21, 2034) is formed by the action of tribromdinitrobenzene upon malonic ester.

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(3) Acids, $C_{10}H_{10}O_4$.

Dimethyl Phthalic Acids, $C_6H_2(CH_3)_2(CO_2H)_2$. Two isomeric acids, called cumidic acids, have been obtained by the oxidation of durene and durylic acids (p. 760) (*Berichte*, 19, 2508).

o-**Hydrocinnamic Carboxylic Acid**, $C_6H_4\left\langle\begin{array}{l}CH_2.CH_2.CO_2H\\ CO_2H\end{array}\right.$ (1, 2), is formed by oxidizing tetrahydro-β-naphthylamine with potassium permanganate. It melts at 165° (*Berichte*, 23, 1562; 21, 1120).

Phenylene Diacetic Acids, $C_6H_4\left\langle\begin{array}{l}CH_2.CO_2H\\ CH_2.CO_2H\end{array}\right.$. The *para*- and *ortho*-acids have been obtained from the xylylene cyanides (p. 735). The first melts at 244°, and the second at 150°.

Phenyl-Succinic Acid, $\begin{array}{l}C_6H_5.CH.CO_2H\\ \qquad\ \ |\\ \quad\ \ CH_2.CO_2H\end{array}$, results from α-chlorstyrene, $C_6H_5.C_2H_3Cl$, by means of potassium cyanide; by the decomposition of phenylacetsuccinic ester, by means of alkalies; from phenyl-ethane-tri-carboxy-succinic acid (p. 797), and from the so-called hydro-cornicularic acid, $C_{17}H_{16}O_8$. It crystallizes from hot water in warty masses, melts at 167° (162°) and (like succinic acid) yields an *anhydride*, $C_{10}H_8O_3$, melting at 54°.

Phenylmalic and phenylmaleïc acids (*Berichte*, 23, Ref. 573) are produced when bromine, etc., acts upon phenylsuccinic acid.

β-**Phenylisosuccinic Acid**, $C_6H_5.CH_2.CH(CO_2H)_2$, Benzyl Malonic Acid, formed from sodium malonic ester, $\mathrm{CH(Na)(CO_2R)_2}$, and benzyl chloride is very readily soluble in water, melts at 117°, and at 180° decomposes into carbon dioxide and hydrocinnamic acid, $\mathrm{C_6H_5.CH_2.CH_2.CO_2H}$.

The ester of *dibenzyl malonic acid*, $\mathrm{(C_6H_5.CH_2)_2C.(CO_2H)_2}$ (*Berichte*, 20, Ref. 380), is produced simultaneously with benzyl-malonic ester by the entrance of a second benzyl group.

The action of *o*- and *p*-nitrobenzyl chloride upon malonic ester produces the corresponding nitrobenzyl- and bi-nitrobenzyl-malonic esters (*Berichte*, 20, 434).

4. **Benzylsuccinic Acid**, $\mathrm{C_6H_5.CH_2.C_2H_3(CO_2H)_2 = C_{11}H_{12}O_4}$, results from ethan-tricarboxylic ester (p. 471), or ethan-tetracarboxylic ester (p. 481), by the action of benzyl chloride, etc. (*Berichte*, 17, 449), as well as by the reduction of phenylitaconic acid (*Berichte*, 23, Ref. 237). It melts at 161° and forms an anhydride, melting at 102°.

Symmetrical benzyl-alkyl-succinic acids, capable of existing in two alloisomeric forms, are similarly produced (*Berichte*, 23, 1942).

OXYDICARBOXYLIC ACIDS AND OXYALDEHYDIC ACIDS.

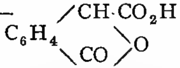
The oxyphthalic acids, $\mathrm{C_8H_6O_5 = C_8H_3(OH).(CO_2H)_2}$, can be obtained from the phthalic acids by the introduction of the OH-group by means of the amido- or sulpho-derivatives. They are also formed from the oxy-monocarboxylic acids, $\mathrm{C_6H_4(OH).CO_2H}$, by heating their alkali salts in a current of carbon dioxide, or by means of the $\mathrm{CCl_4}$ reaction (p. 767). Their ether acids, *e.g.*, $\mathrm{C_6H_3(O.CH_3)(CO_2H)_2}$, result by the oxidation of the ether acids of the oxytoluic acids, $\mathrm{C_6H_3(O.CH_3)}\left\langle\begin{matrix}\mathrm{CH_3}\\ \mathrm{CO_2H}\end{matrix}\right.$ (p. 771), and by the same treatment of the *oxyaldehydic acids*, $\mathrm{C_6H_3(O.CH_3)}\left\langle\begin{matrix}\mathrm{CHO}\\ \mathrm{CO_2H}\end{matrix}\right.$ (the latter are obtained from the oxymonocarboxylic acids, $\mathrm{C_6H_4(OH).CO_2H}$, by means of the $\mathrm{CCl_3H}$ reaction, and by further introduction of methyl); when the phenol ethers are heated with hydrochloric acid the free oxydicarboxylic acids result. Hence, the six possible **Oxyphthalic Acids**, $\mathrm{C_6H_3(OH).(CO_2H)_2}$, can be obtained by these reactions (*Berichte*, 16, 1966).

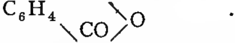
Oxyterephthalic Acid, $\mathrm{C_6H_3(OH)(CO_2H)_2}$, has been obtained from nitroterephthalic acid. It is a powder that dissolves with great difficulty. Sodium amalgam converts it into **Tetrahydro-oxyterephthalic Acid**, $\mathrm{C_6H_7(OH)(CO_2H)_2}$, or $\mathrm{C_6H_8(O)(CO_2H)_2}$, which at 118° (or readily when heated with water) decomposes into carbon dioxide and **Hexahydro-ketobenzoic Acid**, $\mathrm{CO_2H.CH}\left\langle\begin{matrix}\mathrm{CH_2.CH_2}\\ \mathrm{CH_2.CO}\end{matrix}\right\rangle\mathrm{CH_2}$. The latter is a syrup. It forms an oxime with hydroxylamine and a hydrazone with phenylhydrazine. Acids transform the latter into a carbazol derivative (*Berichte*, 22, 2179).

Phenyl-malic Acids, $\begin{array}{c}\mathrm{C_6H_5.C(OH).CO_2H}\\ |\\ \mathrm{CH_2.CO_2H}\end{array}$ and $\begin{array}{c}\mathrm{C_6H_5.CH.CO_2H}\\ |\\ \mathrm{CH(OH).CO_2H}\end{array}$. The first may be obtained from phenylsuccinic acid by the action of bromine and water. It melts at 187°. The second acid is derived from phenyl-formyl acetic ester (p. 761) by the action of CNH, etc. It melts at 150–160° (*Berichte*, 23, Ref. 572).

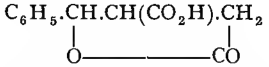
Oxyuvitic Acid, $\mathrm{C_9H_8O_5 = C_6H_2(CH_3)}\left\{\begin{matrix}\mathrm{OH}\\ \mathrm{(COOH)_2}\end{matrix}\right.$, is a homologue of the oxybenzenedicarboxylic acids, and is produced by the action of chloroform, chloral or trichloracetic ester upon sodium aceto-acetic ester (*Annalen*, 222, 258). It crystallizes from hot water in fine needles, and melts with decomposition at about 290°.

The γ-oxybenzene dicarboxylic acids at once eliminate water and become *lactonic acids.* In this class may be included:—

Phthalid-carboxylic Acid, $C_9H_6O_4 = $  $C_6H_4{<}\begin{matrix}CH\cdot CO_2H\\ CO\end{matrix}{>}O$. This is produced by reducing phenyl-glyoxyl-*o*-carboxylic acid (p. 765) with sodium amalgam (*Berichte*, **18**, 381). It is quite soluble in water, crystallizes in leaflets, melts at 149°, and beyond 180° decomposes into carbon dioxide and phthalide.

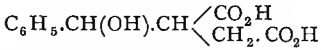
Phthalid-acetic Acid, $C_{10}H_8O_4 = $  $C_6H_4{<}\begin{matrix}CH\cdot CH_2\text{-}CO_2H\\ CO\end{matrix}{>}O$. Derived from benzoyl aceto-carboxylic acid (p. 765) by the action of sodium amalgam. It is very soluble in hot water and alcohol. It crystallizes with one molecule of water in delicate needles, melting at 151°.

Phenyl-paraconic Acid, $C_{11}H_{10}O_4$, and **Phenyl-itamalic Acid**, $C_{11}H_{12}O_5$:—



$$\begin{matrix}C_6H_5.CH.CH(CO_2H).CH_2\\ | \qquad\qquad\qquad\qquad | \\ O\text{—————————}CO\end{matrix}$$

Phenyl-paraconic Acid.



$$C_6H_5.CH(OH).CH{<}\begin{matrix}CO_2H\\ CH_2.CO_2H\end{matrix}$$

Phenyl-itamalic Acid.

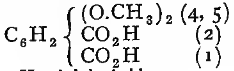
The lactone acid of phenyl-itamalic acid is obtained by heating benzaldehyde with sodium succinate and acetic anhydride. It crystallizes from hot water in shining needles, and melts at 99°; when perfectly anhydrous at 109°. When it is boiled with alkalies it yields the salts of phenyl-itamalic acid. The latter, when in a free condition, immediately reverts to phenyl-paraconic acid. This, upon distillation, breaks down into carbon dioxide, phenylbutyrolactone (p. 777) and phenylisocrotonic acid. A further product is α-naphthol.

Three *chlorparaconic acids* are similarly produced from sodium succinate and the three chlorbenzaldehydes. They yield three chlorinated α-naphthols (*Berichte*, **21**, Ref. 733). Pyrotartaric acid and benzaldehyde (p. 462) yield α- and β-*methyl-phenyl paraconic acid*, $C_{12}H_{12}O_4$, from which methyl-α-naphthol may be produced by distillation (*Berichte*, **23**, Ref. 96). Sodium, or sodium ethylate, acting upon phenyl-paraconic ester, produces *phenyl-itaconic acid*, $C_6H_5.CH{:}CH(CO_2H)CH_2.CO_2H$ (*Berichte*, **23**, Ref. 236), by a reaction peculiar to lactonic acids.

DIOXY-CARBOXYLIC ACIDS.

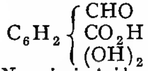
Dioxyphthalic Acids, $C_6H_2(OH)_2(CO_2H)_2$. Eleven isomerides.

1. There are four possible dioxy-acids of ortho-phthalic acid. The most remarkable of these is dioxy-phthalic acid (1, 2, 4, 5—the hydroxyls in 4 and 5). It has not yet been isolated, because it readily loses carbon dioxide and passes into protocatechuic acid (2, 4, 5—CO_2H in 2). The following compounds are among its derivatives; they have been prepared from narcotin: *hemipinic acid*, $C_{10}H_{10}O_6$, *opianic acid*, $C_{10}H_{10}O_5$, *noropianic acid*, $C_8H_6O_5$, *meconinic acid*, $C_{10}H_{12}O_5$, and *meconine*, $C_{10}H_{10}O_4$:—



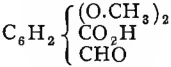
$$C_6H_2\begin{cases}(O.CH_3)_2 & (4, 5)\\ CO_2H & (2)\\ CO_2H & (1)\end{cases}$$

Hemipinic Acid.



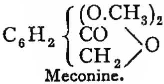
$$C_6H_2\begin{cases}CHO\\ CO_2H\\ (OH)_2\end{cases}$$

Noropianic Acid.



$$C_6H_2\begin{cases}(O.CH_3)_2\\ CO_2H\\ CHO\end{cases}$$

Opianic Acid.



$$C_6H_2\begin{cases}(O.CH_3)_2\\ CO\\ CH_2\end{cases}{>}O$$

Meconine.

Hemipinic Acid, $C_{10}H_{10}O_6$. This should be regarded as a carboxyl derivative of dimethyl protocatechuic acid, since it decomposes, when heated with hydrochloric acid, into protocatechuic acid, carbon dioxide and methyl chloride:—

$$C_{10}H_{10}O_6 + 2HCl = C_7H_6O_4 + CO_2 + 2CH_3Cl.$$

It is formed together with opianic acid and meconine by oxidizing narcotin with dilute nitric acid. In an anhydrous state it melts at 182°, and yields an anhydride, melting at 167°. Hence, the CO_2H groups occupy the ortho-position.

Metahemipinic Acid, isomeric with hemipinic acid, is formed by the oxidation of papaverine (*Berichte*, 21, Ref. 787; 22, Ref. 195).

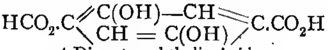
Noropianic Acid, $C_8H_6O_5$, dioxyaldehyde carboxylic acid, aldehydo-protocatechuic acid (see above), is obtained from opianic acid by the elimination of the two methyl groups upon heating with hydriodic acid (isovanillin is simultaneously formed by the removal of one methyl group and carbon dioxide). It is rather readily soluble in water, melts when anhydrous at 171°, and is colored bluish-green by ferric chloride.

Opianic Acid, $C_{10}H_{10}O_5$, the dimethyl ether of the preceding compound, is an aldehyde-dimethyl-protocatechuic acid, because when it is heated with hydrochloric acid it yields protocatechuic aldehyde, carbon dioxide and two molecules of methyl chloride. It is converted into dimethyl-protocatechuic aldehyde when heated with soda-lime. It crystallizes from hot water in fine prisms, melting at 150°. It is oxidized to hemipinic acid. Opianic acid unites with phenylhydrazine with the elimination of two molecules of water (*Berichte*, 19, 763). Consult *Berichte*, 21, 2518, for its combinations with diphenylhydrazine, hydrazobenzene, etc. When opianic acid combines with hydroxylamine, two molecules of water escape, and hemipinimide (*Berichte*, 19, 2278, 2913) is formed. Consult *Berichte*, 19, 2299; 20, 875 for azo-opianic acid derived from nitro-opianic acid.

Meconine, $C_{10}H_{10}O_4$, results when sodium amalgam acts upon opianic acid and the solution is precipitated by acids. At first the sodium salt of **Meconinic Acid**, $C_{10}H_{12}O_5$, is produced. The latter is a γ-oxyacid, and at once parts with water, passing into its lactone anhydride—meconine (see Phthalide, p. 772). Meconine occurs already formed in opium, and is obtained on boiling narcotine with water. It yields shining crystals, melting at 102°, and dissolving with difficulty in water. It dissolves in the alkalies, yielding salts of meconinic acid. In the same manner that phthalimide yields phthalide (p. 788), hemipinimide furnishes ψ-meconine, and not meconine (*Berichte*, 20, 883).

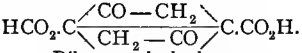
2. The most interesting of the four possible dioxy-acids derived from terephthalic acid is—

***p*-Dioxy-terephthalic Acid**, $C_6H_2(OH)_2(CO_2H)_2$ (1, 4–2, 5), containing the hydroxyl groups in opposite para-positions. It is isomeric or tautomeric with hypothetical diketo-tetrahydro-benzene dicarboyxlic acid:—



$$HCO_2.C{\begin{array}{l}\diagup\!\!\diagup C(OH)-CH\diagdown\!\!\diagdown\\ \diagdown CH=C(OH)\diagup\end{array}}C.CO_2H$$

p-Dioxyterephthalic Acid.



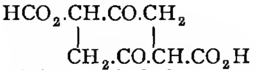
$$HCO_2.C{\begin{array}{l}\diagup CO-CH_2\diagdown\\ \diagdown CH_2-CO\diagup\end{array}}C.CO_2H.$$

Diketo-tetrahydro-benzene Dicarboxylic Acid.

Free dioxyterephthalic acid may be obtained by boiling its ester with sodium hydroxide. It crystallizes from alcohol in yellow leaflets, containing two molecules of water. Ferric chloride imparts a deep blue coloration to its solution. When rapidly distilled it decomposes into two molecules of carbon dioxide and hydroquinone. Sodium amalgam reduces it to succino-succinic acid (*Berichte*, 22, 2168). Its *diethyl ester*, $C_8H_4O_6(C_2H_5)_2$, may be prepared by withdrawing two hydrogen atoms from succino-succinic ester ($C_8H_6O_6(C_2H_5)_2$), by means of bromine or PCl_5 (*Berichte*, 22, 2107), or by the action of sodium ethylate upon dibromacetoacetic ester (*Annalen* 219, 78). It crystallizes in two distinct forms, at the ordinary temperature in yellowish green prisms or plates, at higher temperatures in colorless leaflets. It also sublimes in the latter form. It melts at 133°. In most of its reactions the ester conducts itself like a hydroxyl-derivative. It does not combine with hydroxylamine or phenylhydrazine, and with sodium and alkyl iodides yields dialkyl esters. It, however, does not react with phenylcyanate (p. 613) (*Berichte*, 23, 259), and shows some analogies with succino-succinic ester. Hence, it is considered a quinone- or diketo-derivative—corrresponding to the tautomeric formula given above. The different physical modifications of the ester and analogous compounds, according to Hantzsch, correspond to the two desmotropic conditions (p. 54)—the colored variety agreeing with the quinone formula, while the colorless corresponds to the hydroxyl formula (*Berichte*, 22, 1294). However, the color cannot be regarded as a certain criterion for the distinction of the ketone from the hydroxyl form. Even chemical reactions do not prove that desmotropic forms can be accepted (Nef, *Berichte*, 23, Ref. 585; Goldschmidt, *Berichte*, 23, Ref. 260).

Dioxyterephthalic ester, by reduction (boiling with zinc and hydrochloric acid in alcoholic solution), is again changed to succino-succinic ester (*Berichte*, 19, 432; 22, 2169). A dihydroxamic acid is formed with hydroxylamine hydrochloride; *tetrahydrodioxy-terephthalic acid*, $C_8H_2(H_4)(OH)_2(CO_2H)_2$, is produced at the same time, and decomposes at 180° with carbonization (*Berichte*, 22, 1280).

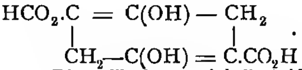
Succino-succinic Acid, $C_8H_8O_6$, may be represented by either of the following formulas:—



$$\begin{array}{l} HCO_2.CH.CO.CH_2 \\ \qquad\quad | \qquad\quad | \\ \qquad\quad CH_2.CO.CH.CO_2H \end{array}$$

p-Diketo-hexahydro-benzene Dicarboxylic Acid.

or



$$\begin{array}{l} HCO_2.C = C(OH) - CH_2 \\ \qquad\quad | \qquad\qquad\qquad | \\ \qquad\quad CH_2 - C(OH) = C.CO_2H \end{array}$$

Dioxy-dihydro-terephthalic Acid.

The first is derived from hexahydrobenzene, the second from $\Delta_{1,4}$-dihydroterephthalic acid (*Berichte*, 22, 2107 and 2169). The *diethyl ester* is produced by the condensation of two molecules of succinic ester through the agency of sodium or sodium ethylate upon succinic ester or bromacetoacetic ester (p. 333) (*Berichte*, 21, 1464; 22, 1282). It crystallizes in bright green triclinic prisms or colorless needles, melting at 126–127°. It is insoluble in water, dissolves with difficulty in ether, very readily in alcohol; its solution shows a bright blue fluorescence. Ferric chloride imparts a cherry red color to it. The *dimethyl ester*, $C_8H_6O_6(CH_3)_2$, from methyl succinic ester, melts at 152°. The esters dissolve in alkalies (not ammonia) with a yellow color. They yield metallic derivatives by the replacement of two hydrogen atoms (*Berichte*, 19, 428).

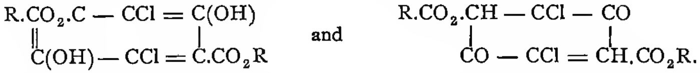
With hydroxylamine (in alkaline or acid solution) succino-succinic ester does not react directly like a diketone, but, splitting off CO_2R and four hydrogen atoms, yields quinone-dioxime carboxylic ester ($C_6H_3(N.OH)_2.CO_2R$), forming yellow needles, melting at 174° (*Berichte*, 22, 1283). The ester appears to form a normal hydrazone with phenylhydrazine (*Berichte*, 19, 429). It does not react with phenylcyanate (*Berichte*, 23, 258). PCl_5 converts the ester into *dichlorhydroterephthalic acid*, $C_6H_4Cl_2(CO_2H)_2$ (*Berichte*, 21, 468).

If succino-succinic ester be saponified by dilute alkalies, with exclusion of air, it yields free

Succino-succinic Acid, $C_8H_8O_6 = C_6H_8O_2(CO_2H)_2$ (see above). This may be more readily obtained by boiling dioxyterephthalic ester with sodium hydroxide and reducing the product with sodium amalgam (*Berichte*, 22, 2168). It is a yellow pulverulent precipitate, which dissolves with difficulty. Air oxidizes it in solution to dioxyterephthalic acid. Water gradually decomposes it into carbon dioxide and *succinylo-propionic acid*, $C_6H_6O_2.CO_2H$. The acid breaks down into two molecules of carbon dioxide and diketohexamethylene upon the application of heat.

Chlorine converts succino-succinic ester and dioxyterephthalic ester into *p*-dichlorquinone-dicarboxylic ester, $CCl_2O_2(CO_2.C_2H_5)_2$. This consists of greenish yellow crystals, melting at 195°. Bromine produces the analogous *dibrom*-derivative (*Berichte*, 21, 1761). Zinc dust and glacial acetic acid yield

Dichlorhydroquinone-dicarboxylic Ester, $C_6Cl_2H_2O_2(CO_2R)_2$, crystallizing in two different forms—colorless needles and yellow-green plates, corresponding to the desmotropic forms (see above) (*Berichte*, 20, 2796):—



$$\begin{array}{l} R.CO_2.C - CCl = C(OH) \\ \quad \| \qquad\qquad\qquad\quad | \\ \quad C(OH) - CCl = C.CO_2R \end{array} \quad \text{and} \quad \begin{array}{l} R.CO_2.CH - CCl - CO \\ \qquad\quad | \qquad\qquad\quad\; | \\ \qquad\quad CO - CCl = CH.CO_2R. \end{array}$$

However, the existence of a chemical difference has not been proven (*Berichte*, 23, 260). **Dibromhydroquinone-dicarboxylic Ester**, $C_6Br_2H_2O_2(CO_2R)_2$ (*Berichte*, 21, 1759), shows a like deportment.

Dioxy-quinone-dicarboxylic Ester, $C_6H_2(OH)_2(CO_2R)_2 = C_8H_2O_8R_2$, may be prepared by shaking dichlorhydroquinone-dicarboxylic ester with sodium hydroxide, and by the action of nitrous acid upon dioxy-terephthalic ester (*Berichte*, 19, 2385). It melts at 151°, and crystallizes in pale yellow leaflets and intense greenish yellow prisms. The latter form is probably diquinoyl-dihydrobenzene dicarboxylic ester, $C_8H_2(O_2)(O_2)(CO_2R)_2$ (*Berichte*, 20, 1307). It reacts acid, and forms salts with two equivalents of the metals. It does not form a dioxime with hydroxylamine, but an oxyammonium salt, and with phenylhydrazine a phenylhydrazine salt (*Berichte*, 22, 1290). Furthermore, it does not react with phenylcyanate (*Berichte*, 23, 265). Boiling hydrochloric acid decomposes the ester into carbon dioxide and dioxy-quinone (p. 702). By the absorption of two atoms of hydrogen (by reduction with sulphurous acid) the ester becomes

Tetroxy-terephthalic Ester, $C_6(OH)_4(CO_2R_2)$, or **Dioxy-quinone-dihydrocarboxylic Ester**, $C_6H_2(O_2)(OH)_2(CO_2R)_2$. It crystallizes in golden yellow leaflets and melts at 178° (*Berichte*, 20, 2798). Its alkaline solution oxidizes on exposure to the air (giving up two hydrogen atoms) to dioxy-quinone-dicarboxylic ester, hence, it yields the same products with hydroxylamine and phenylhydrazine (*Berichte*, 22, 1291). It forms a tetracarbanilido-derivative (*Berichte*, 23, 267) with four molecules of phenylcyanate.

The following is a trioxy-dicarboxylic acid:—

Gallocarboxylic Acid, $C_6H(OH)_3(CO_2H)_2 = C_8H_6O_7$. It may be prepared from pyrogallol by heating it to 180° with ammonium carbonate. Pyrogallo-carboxylic acid is formed at the same time. It dissolves in water with difficulty, crystallizes in needles, and melts at 270° with decomposition.

TRIBASIC ACIDS.

Benzene Tricarboxylic Acids, $C_6H_3(CO_2H)_3$, 3 isomerides.

1. **Trimesic Acid**, $C_9H_6O_6$ (1, 3, 5), is formed when mesitylenic and uvitic acids are oxidized with a chromic acid mixture (mesitylene is at once burnt up); by heating mellitic acid with glycerol (together with tetracarboxylic acids), or hydro- and isohydromellitic acid with sulphuric acid. The synthetic methods for its production are: heating benzene trisulphonic acid with potassium cyanide and saponifying the resulting cyanide (p. 660); by polymerizing propiolic acid (p. 565); and by the action of sodium upon a mixture of acetic and formic esters (p. 566). It crystallizes in short prisms, which dissolve readily in hot water and alcohol. It melts about 300°, and sublimes near 240°. Heated with lime it decomposes into $3CO_2$ and benzene. Its *triethyl ester* melts at 132°.

2. **Trimellitic Acid**, $C_6H_3(CO_2H)_3$ (1, 2, 4). This is obtained (together with isophthalic acid) by heating hydropyro-mellitic acid with sulphuric acid, or upon oxidizing xylidic acid with potassium permanganate. It is prepared most readily (along with isophthalic acid) by oxidizing colophony with nitric acid (*Annalen*, 172, 97), is very soluble in water, and separates in warty masses. It melts at 216°, decomposing into water and the anhydride, $C_6H_2(CO_2H)(CO)_2O$. The latter melts at 158°.

3. **Hemimellitic Acid**, $C_6H_3(CO_2H)_3$ (1, 2, 3). This is formed on heating hydromellophanic acid (below) with sulphuric acid. It forms needles, which are sparingly soluble in water, melts at 185°, and decomposes into phthalic anhydride and benzoic acid.

Phenyl-ethenyl-tricarboxylic Acid, $C_6H_5.CH(CO_2H).CH(CO_2H)_2$ (vide p. 471), is obtained from phenylchloracetic ester, $C_6H_5.CHCl.CO_2R$, by the action of sodium malonic ester, $CHNa(CO_2R)_2$. It is a crystalline mass, easily soluble in water, and at 191° decomposes into carbon dioxide and phenyl succinic acid (p. 791) (*Berichte*, 23, Ref. 573).

TRIOXY-TRICARBOXYLIC ACIDS.

Phloroglucin-tricarboxylic Acid, $C_9H_6O_9 = C_6(OH)_3(CO_2H)_3$ or $C_6H_3O_3(CO_2H)_3$ (p. 695), belongs to this class. Its *triethyl ester* may be formed by the condensation of malonic ester upon heating its sodium compound to 120–145° (p. 566), or by the action of zinc alkyl. The ester, $C_9H_3(C_2H_5)_3O_9$, crystallizes from alcohol in yellow needles. These melt at 104°. It dissolves in ether with a greenish fluorescence. It deports itself quite like succino-succinic ester, dissolves unchanged in alkalies, and is colored a cherry-red by ferric chloride. Acetic anhydride converts it into a triacetyl derivative, and with hydroxylamine it yields a trioxime, $C_6H_3(N.OH)_3(CO_2R)_3$ (*Berichte*, 21, 1766), with phenyl cyanate it forms a tricarbamido-derivative (*Berichte*, 23, 270). Fused with alkalies it forms phloroglucin.

TETRABASIC ACIDS.

Benzene Tetracarboxylic Acids, $C_6H_2(CO_2H)_4$. There are three isomerides.

1. **Pyromellitic Acid**, $C_{10}H_6O_8$ (1, 2, 4, 5). Its anhydride is produced when mellitic acid is distilled, or better, when the sodium salt is subjected to the same treatment with sulphuric acid (1½ parts):—

$$C_6(CO_2H)_6 = C_6H_2(CO_2H)_4 + 2CO_2 \text{ and}$$
$$C_6H_2(CO_2H)_4 = C_6H_2(CO)_4O_2 + 2H_2O.$$

The acid results when the anhydride is boiled with water. It is also produced by oxidizing durene and durylic acid with potassium permanganate.

Pyromellitic acid is very similar to phthalic acid. It crystallizes in prisms, containing $2H_2O$, and dissolves readily in hot water and alcohol. At 100° it loses its water of crystallization, melts at 264°, and decomposes into water and the *dianhydride*, $C_{10}H_2O_6 = C_6H_2\left(\begin{matrix}CO\\CO\end{matrix}\!>\!O\right)_2$, which sublimes in long needles, and melts at 286°. The *ethyl ester*, $C_6H_2(CO_2.C_2H_5)_4$, melts at 53°.

Hydro- and *iso-hydro-pyro-mellitic acids*, $C_{10}H_{10}O_8 = C_6H_2(H_4)(CO_2H)_4$, are obtained by the continued action of sodium amalgam upon the aqueous solution of the ammonium salt. The first results as a gummy mass upon evaporating the ethereal solution; it is very soluble in water. The second crystallizes with $2H_2O$, loses the same about 120°, melts near 200°, and decomposes into water, carbon dioxide and Δ_1-tetrahydrophthalic anhydride (p. 788) (*Annalen*, 258, 205). When heated with sulphuric acid both evolve CO_2 and SO_2 and form trimellitic and isophthalic acids.

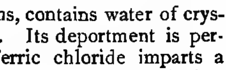
By replacing the two *p* hydrogen atoms in pyromellitic ester by O_2 (by oxidizing the diamido-compound with nitric acid) (*Berichte*, 19, 516) we obtain

Quinone Tetracarboxylic Ester, $C_6(O_2)(CO_2.C_2H_5)_4$, crystallizing in quinone-yellow needles, melting at 148°–150°. It is odorless, but sublimes quite readily. Zinc reduces it in glacial acetic acid solution to

Hydroquinone Tetracarboxylic Ester, $C_6(OH)_2(CO_2.C_2H_5)_4$ or $C_6H_2(O_2)(CO_2.C_2H_5)_4$, crystallizing in bright yellow needles, melting at 126–128° (*Berichte*, 22, Ref. 289). Its solutions exhibit a beautiful blue fluorescence. It dissolves with a yellowish red color in caustic soda. Nitric acid readily reoxidizes it to the quinone-acid. In its entire deportment it shows great analogy to dioxyterephthalic ester (p. 794). In alcoholic solution it is reduced by zinc dust and hydrochloric acid to

Quinone-tetrahydro-tetracarboxylic Ester, $C_6H_4(O_2)(CO_2.C_2H_5)_4$ or

***p*-Diketohexamethylene-tetracarboxylic Ester**, [R = $CO_2.C_2H_5$].



$$CO\begin{matrix}\diagup CHR—CHR \diagdown\\ \diagdown CHR—CHR \diagup\end{matrix}CO$$

It crystallizes from alcohol in *colorless* needles or prisms, contains water of crystallization, softens at 110°, and then melts at 142–144°. Its deportment is perfectly analogous to that of succino-succinic ester. Ferric chloride imparts a cherry-red color to its alcoholic solution. Bromine changes it again to hydroquinone tetracarboxylic ester.

2. **Prehnitic Acid**, $C_{10}H_6O_8$, (1, 2, 3, 4) results (together with mellophanic acid and trimesic acid) upon heating hydro- and isohydro-mellitic acid (p. 800) with sulphuric acid, also by oxidizing prehnitol (p. 576) with potassium permanganate (*Berichte*, 21, 907). It is very soluble in water, and crystallizes in warty masses containing $2H_2O$, and melting at 238° with the formation of an anhydride. Its salts crystallize with difficulty.

Sodium amalgam acting upon the ammonium salt solution, produces *Hydro-*

prehnitic acid, $C_{10}H_{10}O_8$, an amorphous, very soluble mass, which yields prehnitic acid and isophthalic acid when it is heated with sulphuric acid.

3. **Mellophanic Acid**, $C_6H_2(CO_2H)_4$ (1, 2, 3, 5), is formed together with prehnitic acid from hydro- and isohydromellitic acid, and also by the oxidation of isodurene (*Berichte*, 17, 2517). It is also very soluble in cold water and crystallizes in small prisms. It melts at 240° with decomposition into water, and an anhydride melting at 238°.

Benzene Pentacarboxylic Acid, $C_6H(CO_2H)_5$, is produced by oxidizing penta-methylbenzene with permanganate. It is an amorphous powder containing six molecules of water.

HEXABASIC ACIDS.

Mellitic Acid, $C_{12}H_6O_{12} = C_6(CO_2H)_6$. This occurs in *mellite* or *honey-stone*, which is found in some lignite beds. Honey-stone is an aluminium salt of mellitic acid, $C_{12}Al_2O_{12} + 18H_2O$, and affords large quadratic pyramids of a bright yellow color.

In preparing the acid, honeystone is boiled with ammonium carbonate, ammonium hydroxide added, and the separated aluminium hydroxide filtered off. The ammonium salt, $C_{12}(NH_4)_6O_{12} + 9H_2O$, crystallizes from the filtrate in large rhombic prisms, which effloresce in the air. The free acid is obtained by conducting chlorine into the aqueous solution of the ammonium salt (*Berichte*, 10, 560).

An interesting formation of mellitic acid is that whereby pure carbon (graphite, charcoal, etc.) is oxidized with an alkaline solution of potassium permanganate. Another is when the carbon is applied as positive electrode in electrolysis (*Berichte*, 16, 1209; 17, Ref. 701).

Mellitic acid crystallizes in fine, silky needles, readily soluble in water and alcohol. It is very stable, and is not decomposed by acids, by chlorine or bromine, even upon boiling. When heated it melts and decomposes into water, carbon dioxide and pyromellitic anhydride. It yields benzene when distilled with lime.

Mellitic acid forms salts with six equivalents of metal. The *calcium* and *barium*, $C_{12}Ba_3O_{12} + 3H_2O$, salts are insoluble in water. The *methyl ester*, $C_6(CO_2.CH_2)_6$, crystallizes in leaflets, melting at 187°; the *ethyl ester* melts at 73°. Phosphorus pentachloride produces chloranhydrides.

The known amides of mellitic acid are *Paramide* and *Euchroic Acid;* they appear in the dry distillation of the ammonium salt.

Paramide or *Mellimide*, $C_{12}H_3N_3O_6 = C_6\left(\begin{matrix}CO\\CO\end{matrix}>NH\right)_3$, is a white, amorphous powder, insoluble in water and alcohol. Heated to 200° with water, it is converted into the tertiary ammonium salt of mellitic acid. The alkalies convert paramide into euchroic acid.

Euchroic Acid, $C_{12}H_4N_2O_8 = C_6\left(\begin{matrix}CO\\CO\end{matrix}>NH_2\right)\left\{\begin{matrix}CO.OH\\CO.OH\end{matrix}\right.$, crystallizes in large prisms, and is sparingly soluble in water. Heated with water to 200° it yields mellitic acid. Nascent hydrogen changes euchroic acid to *euchrone*, a dark blue precipitate, which reverts to colorless euchroic acid upon exposure. Euchrone dissolves with a dark red color in alkalies.

Sodium amalgam acting on ammonium mellitate produces *Hydromellitic Acid*, $C_{12}H_6(H_6)O_{12}$. This is very soluble in water and alcohol, sparingly in ether, and is indistinctly crystalline. It melts with decomposition. It is hexabasic, its calcium salt being more soluble in cold than in hot water. If the acid be heated to 180° with concentrated hydrochloric acid, or if it be preserved, it is transformed into the isomeric *Isohydromellitic Acid*, $C_{12}H_{12}O_{12}$, crystallizing in large, six-sided prisms. Hydrochloric acid precipitates it from its aqueous solution.

When more highly heated with sulphuric acid, both acids yield prehnitic acid, mellophanic acid and trimesic acid:—

$$C_6H_6(CO_2H)_6 = C_6H_2(CO_2H)_4 + 3H_2 + 2CO_2,$$

and

$$C_6H_6(CO_2H)_6 = C_6H_3(CO_2H)_3 + 3H_2 + 3CO_2.$$

UNSATURATED COMPOUNDS.

The benzene derivatives previously studied contain saturated side-chains, having carbon present in them. Perfectly analogous compounds exist, in which unsaturated side-chains are present:—

$C_6H_5.CH{:}CH_2$. Phenyl-ethylene, Styrolene.	$C_6H_5.CH{:}CH.CO_2H$. Phenyl-acrylic Acid, Cinnamic Acid.
$C_6H_5.CH_2.CH{:}CH_2$ Phenyl-allyl.	$C_6H_5.CH_2.CH{:}CH.CO_2H$ Phenyl-crotonic Acid.
$C_6H_5.C{\equiv}CH$ Phenyl-acetylene.	$C_6H_5.C{\equiv}C.CO_2H$, etc. Phenyl-propiolic Acid.

Hydrogen converts them into the corresponding saturated compounds.

Hydrocarbons.

Phenyl Ethylene, $C_8H_8 = C_6H_5.CH{:}CH_2$, **Styrolene,** Vinylbenzene, occurs in storax (808) (1–5 per cent.), from which it is obtained upon distillation with water. It is prepared by the action of zinc dust and glacial acetic acid upon phenylacetylene. Sodium and methyl alcohol will produce the same result (two hydrogen atoms are added) (*Berichte*, **21**, 1184); by heating cinnamic acid with lime or with water to 200°; by the action of alcoholic potash upon brom-ethyl benzene, and by the condensation of acetylene, C_2H_2, upon application of heat. It is best obtained from β-brom-hydro-cinnamic acid (p. 757), which is immediately decomposed by a soda solution into styrolene, carbon dioxide and hydrobromic acid (*Berichte* **15**, 1983). It is a mobile, strongly refracting liquid, with an agreeable odor. Pure styrolene is optically inactive and boils at 144–145°; its sp. gr. = 0.925 at 0°.

Hydriodic acid converts styrolene into ethyl benzene, $C_6H_5.C_2H_5$; chromic acid or nitric acid oxidizes it to benzoic acid.

Being an unsaturated compound, styrolene can directly take up two halogen atoms, forming *αβ*-derivatives of ethylbenzene. It condenses with phenol, on boiling with sulphuric acid, to oxy-diphenyl ethane, $C_6H_5.C_2H_4.C_6H_4.OH$ (*Berichte*, 23, 3145).

Two series of mono-substitution products result when the hydrogen of the side-chain of styrolene suffers replacement:—

$C_6H_5.CH:CHBr$	and	$C_6H_5.CBr:CH_2$.
α-Brom-styrolene.		β-Brom-styrolene.

The *α-products* are derived (along with phenylacetaldehyde) from the phenyl-α-chlor (brom-) lactic acid (p. 776), upon heating with water. They are oils having a hyacinth-like odor, boil undecomposed, and are far less reactive than the β-products (similar to the halogen propylenes). α-**Chlor-styrolene**, $C_6H_5.CH:CHCl$, is obtained from α-dichlor-ethyl-benzene (p. 586), and boils at 199°. α-**Brom-styrolene** is formed from dibrom-hydrocinnamic acid (p. 757), by boiling with water or digesting with a soda solution. It melts at 7° and boils at 220°. When it is heated with water it yields phenyl-acetaldehyde, $C_6H_5.CH_2.CHO$.

The *β-products* result on heating styrolene chloride (-bromide), $C_6H_5.C_2H_3Cl_2$, alone, with lime or with alcoholic potash. They do not distil undecomposed, and possess a penetrating odor, causing tears. They yield acetophenone, $C_6H_5.CO.CH_3$ (*Berichte*, 14, 323), when they are heated with water (to 180°) or with sulphuric acid. β-**Chlor-styrolene**, $C_6H_5.CCl:CH_2$, also results from β-dichlorethyl benzene (p. 586), when it is digested with alcoholic potash. β-**Brom-styrolene** yields phenyl acetylene with alcoholic potash at 120°; sodium and carbon dioxide convert it into phenyl-propiolic acid.

Nitro-styrolenes.

α-**Nitro-styrolene**, $C_6H_5.CH:CH(NO_2)$, phenylnitro-ethylene, is obtained by boiling styrolene with fuming nitric acid, by heating benzaldehyde to 190° with nitromethane, $CH_3(NO_2)$, and $ZnCl_2$ to 190° (*Berichte*, 17, Ref. 527), and by the action of fuming nitric acid upon phenyl-isocrotonic acid (*Berichte*, 17, 413), as well as by the action of NO_2 upon cinnamic acid, when the dinitro-compound, $C_6H_5.C_2H_2(NO_2)_2.CO_2H$, formed at first, decomposes (*Berichte*, 18, 2438). It possesses a peculiar odor, provoking tears, is readily volatilized in aqueous vapor, and yields yellow needles, melting at 58°. Dilute nitric acid decomposes it into benzaldehyde, carbon monoxide and hydroxylamine.

The *nitro-styrolenes*, $C_6H_4(NO_2).CH:CH_2$ (*o*-, *m*- and *p*), containing the nitro-group in the benzene nucleus, result from the nitrophenyl-β-brom-lactic acids (from the three nitro-cinnamic acids, p. 764), by the action of a soda solution in the cold, or upon boiling the β-lactones obtained from the phenyl-brom-lactic acids with water (*Berichte*, 16, 2213, 17, 595). **Orthonitro-styrolene** melts at 13°, has a peculiar odor, and is colored blue by sulphuric acid. **Meta-nitro-styrolene** melts at —5°, **para-nitro-styrolene** at 29°; both have an odor like that of cinnamic aldehyde.

o-**Nitro-chlor-styrolene**, $C_6H_4(NO_2).CH:CHCl$, is produced in the preparation of *o*-nitro-phenyl-chlor-lactic acid and melts at 59° (*Berichte*, 17, 1070).

Dinitro-styrolene, $C_6H_4(NO_2).CH:CH(NO_2)$, results from *p*-α-dinitro-cinnamic acid (p. 811), by the splitting off of CO_2; it consists of yellow leaflets, melting at 199°. When it is heated to 100° with sulphuric acid it is broken up into *p* nitrobenzaldehyde, carbon monoxide and hydroxylamine (*Berichte*, 17, Ref. 528).

Amido-styrolenes.

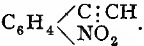
o-**Amido-chlor-styrolene**, $C_6H_4(NH_2).CH:CHCl$, is obtained by reducing *o*-nitro-chlor-styrolene (see above) with tin and hydrochloric acid; it consists of white prisms. Heated to 170° with sodium alcoholate it yields indol, C_8H_7N.

p-**Amido-styrolene**, $C_6H_4(NH_2).CH:CH_2$, is produced (together with *p*-amido-cinnamic acid) in the reduction of *p*-nitro-cinnamic ester; it melts about 81°.

Phenyl Acetylene, $C_6H_5.C \vdots CH$, acetenyl benzene, is produced when *β*-brom-styrolene and acetophenone chloride, $C_6H_5.CCl_2.CH_3$, are heated to 130° with alcoholic potash; also from phenyl-propiolic acid (p. 814), on heating it with water to 120°, or upon distilling the barium salt:—

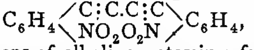
$$C_6H_5.C \vdots C.CO_2H = C_6H_5.C \vdots CH + CO_2.$$

It is a pleasant-smelling liquid, boiling at 139–140°. It forms metallic compounds, like acetylene, with ammoniacal silver and copper solutions: $(C_8H_5)_2Cu_2$, is bright yellow, $(C_6H_5)_2Ag_2 + Ag_2O$ is white. The sodium compound, C_8H_5Na, inflames in the air, and with carbon dioxide it yields propiolic acid. When phenyl-acetylene is dissolved in sulphuric acid and diluted with water, it yields aceto-phenone (see p. 726).

o-**Nitrophenyl Acetylene**,  $C_6H_4\begin{cases} C \vdots CH \\ NO_2 \end{cases}$. This is produced on boiling nitro-phenylpropiolic acid with water. It forms needles, melting at 81–82°, and yields metallic compounds with Cu and Ag.

p-**Nitrophenyl Acetylene**, $C_8H_4(NO_2).C:CH$, from *p*-nitro-phenylpropiolic acid, melts at 152°.

o-**Amidophenyl Acetylene**, $C_6H_4(NH_2)C \vdots CH$, is produced in the reduction of *o*-nitrophenyl-acetylene with zinc dust and ammonia, or with ferrous sulphate and potassium hydroxide, and in the decomposition of *o*-amido-phenylpropiolic acid. It is an oil with an odor resembling that of the indigo vat. Sulphuric acid and water convert it into *o*-amido-acetophenone.

Phenyl-diacetylene, $C_6H_5.C \vdots C.C \vdots C.C_6H_5$. This arises on shaking the copper derivative of phenyl acetylene in the air (with some ammonia) or more readily by the action of alkaline potassium ferricyanide (*Berichte*, 15, 57). It crystallizes from alcohol in long needles, melting at 97°, combines with eight atoms of bromine and does not form metallic derivatives. *It is the parent hydrocarbon of indigo-blue.* Its *o*-dinitro-derivative,  $C_6H_4\begin{matrix} \diagup C \vdots C.C \vdots C \diagdown \\ \diagdown NO_2\ O_2N \diagup \end{matrix}C_6H_4$, obtained from *o*-nitro-phenyl acetylene copper, by means of alkaline potassium ferricyanide and melting at 212°, yields isomeric *diisatogene*, $C_{16}H_8N_2O_4$, with sulphuric acid. Ammonium sulphide at once converts this into indigo-blue, $C_{18}H_{10}N_2O_2$ (*Berichte*, 15, 53).

Phenyl Allylene, $C_8H_5.C \vdots C.CH_3$, has been obtained from phenylbrom-propylene, $C_6H_5.C_3H_4Br$ (from *α*-methylcinnamic acid, p. 814). It is a liquid with a disagreeable odor. It boils at 185° (*Berichte*, 21, 276).

Phenols.

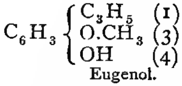
1. **Vinyl Phenols,** $C_6H_4\Big\langle{}^{C_2H_3}_{OH}$. The *methyl ethers* of the *o*- and *p*-compounds, the *vinyl anisols*, $C_6H_4(C_2H_3).O.CH_3$ have been obtained from the corresponding oxycinnamic acids. *o*-Vinyl anisol boils about 198°, the *p*-compound at 205°.

2. **Allyl Phenols,** $C_6H_4\Big\langle{}^{C_3H_5}_{OH}$. *Chavicol*, the para-derivative, occurs in the oil obtained from the leaves of *Chavica Betle*. It is a colorless oil with peculiar odor and boils at 237°. It is not colored by ferric chloride. Its specific gravity is 1.035 at 20°. Its alkyl ethers are produced by heating it with caustic alkali and alkyl iodides. *Methyl Chavicol*, $C_6H_4(C_3H_5)O.CH_3$, boils at 226°; its specific gravity is 0.986 at 22°. *Ethyl Chavicol* boils at 232° (*Berichte*, 22, 2739).

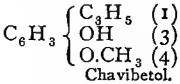
3. **Propenyl Phenols,** $C_6H_4(C_3H_5).OH$, containing the propenyl group—$CH{:}CH.CH_3$. *Anol*, the para-compound, may be obtained from its methyl ether, anethol, by heating it together with caustic alkali to 200–230°. It consists of brilliant leaflets, melting at 92°. It decomposes upon distillation. Its *methyl ether*, $C_6H_4(C_3H_5).O.CH_3$, **anethol**, occurs in ethereal oils, from which it separates in the cold in the form of white, shining scales, melting at 21° and boiling at 232°. Anethol has been synthetically prepared from *p*-methoxyphenyl crotonic acid (*Berichte*, 10, 1604). This would prove the group, C_3H_5, to be propenyl. A rather remarkable formation of anethol is that resulting from the molecular rearrangement of methyl chavicol (see above), when the latter is heated with alcoholic potash. In this change the allyl group is transposed to the propenyl group. *All allyl benzene derivatives sustain similar transformations into propenyl compounds* (*Berichte*, 23, 859); safrol is converted into isosafrol, methyl eugenol into methyl isoeugenol, apiol into isapiol etc., etc. The propenyl derivatives are distinguished from the allyl compounds by higher specific gravities, higher boiling points and greater refractive power (*Berichte*, 22, 2747; 23, 862).

Chromic acid oxidizes anethol to anisic and acetic acids; less intense oxidation produces anisic aldehyde.

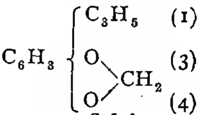
4. **Allyl Dioxybenzenes,** $C_6H_3(C_3H_5)(OH)_2$. There are six possible isomerides; the (1, 3, 4)-compound is known in its ethers:—


$C_6H_3\left\{\begin{array}{ll} C_3H_5 & (1) \\ O.CH_3 & (3) \\ OH & (4) \end{array}\right.$

Eugenol.


$C_6H_3\left\{\begin{array}{ll} C_3H_5 & (1) \\ OH & (3) \\ O.CH_3 & (4) \end{array}\right.$

Chavibetol.

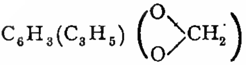


Safrol.

Eugenol, $C_{10}H_{12}O_2$ (Eugenic Acid), occurs in clove oil (from Caryophyllus aromaticus), in all-spice (from Myrtus pimenta). On shaking oil of cloves with alcoholic potassium hydroxide it solidifies to the potassium salt of eugenol; this is then pressed, washed with alcohol, and decomposed with an acid. It is an aromatic oil, that boils at 247°, and is colored blue by ferric chloride. Potassium permanganate oxidizes it to homovanillin, vanillin and vanillinic acid. It breaks down into acetic acid and protocatechuic acid, $C_6H_3(CO_2H)(OH)_2$ (1, 3, 4), when fused with potassium hydroxide (p. 779).

Methyl Eugenol, $C_6H_3(C_3H_5)(O.CH_3)_2$, is formed when eugenol is heated together with caustic potash and methyl iodide. It is a liquid, boiling at 237–239°. Chromic acid oxidizes it to dimethyl protocatechuic acid. The compound, $C_6H_3(C_3H_5)(O.CH_3)_2$, the chief constituent of the *oil of asarum*, appears to be identical with methyl eugenol (*Berichte*, 22, 3172).

Chavibetol, $C_6H_3(C_3H_5)(OH)(O.CH_3)$ (1, 3, 4) (see above), occurs with chavicol in oil of betel (*Berichte*, 23, 859), and is isomeric with eugenol.

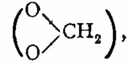


Safrol, $C_{10}H_{10}O_2 = C_6H_3(C_3H_5)\left(\begin{matrix}O\\O\end{matrix}>CH_2\right)$ (see above), is the methylene ether of allyl dioxybenzene. It is present in the oil of *Sassafras officinalis* and *Ilicium religiosum*, hence called *Shikimol*. When the oil is chilled it separates as a white crystalline mass, melting at + 8°. Potassium permanganate oxidizes it to piperonal and piperonylic acid (*Berichte*, 21, 474; 23, 864).

5. Isoeugenol, ethyl isochavibetol and isosafrol are derivatives of—

Propenyl Dioxybenzene, $C_6H_3(C_3H_5)(OH)_2$ (containing the propenyl group—$CH{:}CH.CH_3$), isomeric with allyl dioxybenzene. These can be formed by the rearrangement of corresponding allyl derivatives upon heating the latter with alcoholic potash.

Isoeugenol, $C_6H_3(C_3H_5)(O.CH_3).OH$, is formed when homoferulic acid is distilled with lime. It is an oil boiling at 260° (*Berichte*, 23, 860).



Isosafrol, $C_6H_3(C_3H_5)\left(\begin{matrix}O\\O\end{matrix}>CH_2\right)$, is obtained from safrol by heating it with sodium, or more readily by boiling it with alcoholic soda (*Berichte*, 23, 1160). It is an oil boiling at 246–248°. Chromic acid oxidizes it chiefly to piperonal (artificial *heliotropine*). Sodium and alcohol reduce it to dihydrosafrol and *m*-propyl phenol.

6. **Asarone**, $C_{12}H_{16}O_3 = C_6H_2(C_3H_5)(O.CH_3)_3$, is a derivative of *propenyl trioxybenzene*. It is the solid component of the oil from *Asarum europæum*, whereas the liquid portion consists of methyl eugenol and terpenes (*Berichte*, 21, 615, 1057; 22, 3172). Asarone forms monoclinic prisms, melting at 61° (67°), and boils at 295°. Potassium permanganate oxidizes it to tri-methoxybenzoic acid, $C_6H_2(O.CH_3)_3.CO_2H$, which yields carbon dioxide and the tri-methyl ether of oxyhydroquinone upon distillation with lime (*Berichte*, 23, 2294).

7. **Apiol**, $C_{12}H_{14}O_4 = C_6H(C_3H_5)(O_2{:}CH_2)(O.CH_3)_2$, is a derivative of allyl tetroxybenzene, $C_6H(C_3H_5)(OH)_4$—its methylene dimethyl ester. It occurs in parsley seeds and is volatile in a current of steam. It crystallizes in long needles, with a slight parsley odor. It melts at 30°, and boils at 294°. It dissolves with a blood-red color in oil of vitriol. Potassium permanganate oxidizes it to *apiol aldehyde* and *apiolic acid*, $C_6H(O_2{:}CH_2)(O.CH_3)_2.CO_2H$, melting at 175° (*Berichte*, 21, 1624). When heated with dilute sulphuric acid to 140° apiolic acid breaks down into carbon dioxide and *apione*, the methylene dimethyl ether of apionol, *i. e.*, of tetroxybenzene (*Berichte*, 23, 2293).

Boiling alcoholic potash converts apiol into its isomeric *propenyl*-derivative—*Isapiol* (p. 803). The latter forms leaflets, melts at 56°, and boils at 304°. Potassium permanganate or potassium bichromate and sulphuric acid convert it into apiol aldehyde (*Berichte*, 23, 2293).

Alcohols and Aldehydes.

Styryl Alcohol, $C_9H_{10}O = C_6H_5.CH{:}CH.CH_2.OH$ (Styrene, Cinnamyl Alcohol), is obtained by saponifying styracine, its cinnamic ester, with potassium hydroxide. It crystallizes in shining needles, is sparingly soluble in water, possesses a hyacinth-like odor, melts at 33°, and distils at 250°. When carefully oxidized it becomes cinnamic acid, but in case the oxidation is energetic, benzoic acid is the product. In the presence of platinum sponge it oxidizes in the air to cinnamic aldehyde. It yields cinnamic ether $(C_9H_9)_2O$—a mobile oil—when it is digested with boric anhydride.

Cinnamic Aldehyde, C_9H_8O, is the chief ingredient of the essential oil of cinnamon and cassia (from *Persea Cinnamonum* and *Persea Cassia*). It is obtained by the oxidation of cinnamic alcohol, by dry distillation of a mixture of calcium cinnamate and formate, and by saturating a mixture of benzaldehyde and acetaldehyde with hydrochloric acid, or by the action of caustic soda (pp. 716, 806):—

$$C_6H_5.COH + CH_3.COH = C_6H_5.CH:CH.CHO + H_2O.$$

Sodium ethylate is preferable to aqueous or alcoholic sodium hydroxide for condensation purposes (*Berichte*, **20**, 657).

To obtain the aldehyde from cinnamon oil, shake the latter with a solution of primary sodium sulphite, wash the crystals which separate with alcohol, and decompose them with dilute sulphuric acid (*Berichte*, 17, 2109). Cinnamic aldehyde is obtained synthetically by allowing a mixture of benzaldehyde (10 parts), acetaldehyde (15 parts), water (900 parts), and 10 per cent. ordinary sodium hydroxide to stand and then extracting with ether (*Berichte*, 17, 2117).

Cinnamic aldehyde is a colorless, aromatic oil, which sinks in water and boils at 247°; it distils readily in aqueous vapor. When exposed to the air it oxidizes to cinnamic acid, and in other respects shows all the properties of the aldehydes.

Dry ammonia converts it into the crystalline base **Hydro-cinnamide**, $(C_9H_8)_3N_2$ (p. 715) (*Berichte*, 17, 2110).

Its *phenylhydrazone*, $C_6H_5.CH:CH.CH(N_2H.C_6H_5)$, melts at 168°.

Nitrocinnamic Aldehydes, $C_6H_4(NO_2).CH:CH.CHO$. *Ortho-* and *para-* derivatives are produced by the nitration of cinnamic aldehyde when added to a cold mixture of sulphuric acid (500 gr.) and nitre (20 gr). They can be separated by means of sodium bisulphite (*Berichte*, 18, 2335). The three isomerides can be synthesized by the condensation of the nitrobenzaldehydes with acetaldehyde, induced by caustic soda. By using dilute alkali nitrophenyl-lactic aldehydes are the first products; heated with acetic anhydride they become nitrocinnamic aldehydes.

The *ortho* acid crystallizes from hot water in long needles, melting at 270° (Preparation, *Berichte*, 18, 2335). The *meta* acid melts at 116°, the *para* at 142°. See *Berichte*, 20, 193, for the cumaric aldehydes.

Ketones.

Benzylidene Acetone, $C_6H_5.CH:CH.CO.CH_3$, Benzal Acetone, Cinnamyl-methyl ketone, is obtained on distilling calcium cinnamate and acetate. It is very easily procured by the condensation of benzaldehyde with acetone (p. 716) on shaking with dilute sodium hydroxide (*Annalen*, **223**, 139):—

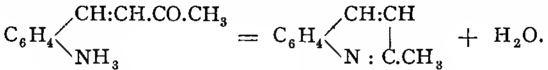
$$C_6H_5.CHO + CH_3.CO.CH_3 = C_6H_5.CH:CH.CO.CH_3 + H_2O.$$

It separates as a thick oil which solidifies after distillation. It has a peculiar odor, crystallizes in brilliant quadratic plates, melts at 41–42°, and boils near 262°. It dissolves in sulphuric acid with an orange-red color, and combines with sodium bisulphite.

Phenylhydrazine converts it into a *hydrazone*, $C_6H_5.CH:CH.C(HN_2.C_6H_5).CH_3$; the rearrangement of this compound gives rise to diphenylmethylpyrazoline (*Berichte*, 21, 1097). Boiling sodium hypochlorite converts benzalacetone into cinnamic acid. Chloroform is eliminated at the same time.

The nitration of benzalacetone with sulphuric acid and nitric acid in the cold produces the ortho- and para-nitro-derivatives; these can be separated by means of alcohol (*Berichte*, 16, 1954).

o-**Nitrobenzal Acetone**, $C_6H_4(NO_2).CH:CH.CO.CH_3$, forms warty crystals, melting at 59°. The action of alcoholic potash, hydrochloric acid, and then sodium hydroxide produces *indigo* (see below). α-Methyl-quinoline results from it by reduction with stannous chloride and hydrochloric acid (p. 755 and p. 721):—



$$C_6H_4\left\langle\begin{matrix}CH:CH.CO.CH_3\\ NH_3\end{matrix}\right. = C_6H_4\left\langle\begin{matrix}CH:CH\\ \quad|\\ N:C.CH_3\end{matrix}\right. + H_2O.$$

α-Methyl Quinoline.

p-**Nitrobenzal Acetone**, melts at 254° (*Berichte*, 16, 1970).

Dibenzylidene Acetone, $\left.\begin{matrix}C_6H_5.CH:CH\\ C_6H_5.CH:CH\end{matrix}\right\rangle CO$ (**Cinnamone**), is produced by the condensation of benzylidene acetone (see above) with benzaldehyde, caused by the action of sodium hydroxide in alcoholic solution. It crystallizes in bright yellow needles, and melts at 112°.

Benzylidene Acetophenone, $C_6H_5.CH:CH.CO.C_6H_5$, is formed when benzaldehyde and acetophenone are allowed to stand together with sodium ethylate (*Berichte*, 20, 657). It crystallizes in prisms or plates, melting at 58° and distilling about 346°.

Acids.

In addition to the general methods for preparing aromatic acids (p. 739) and for the conversion of saturated into unsaturated acids (p. 234), we can also prepare the unsaturated aromatic acids synthetically, by the following methods:—

(1) By the condensation of aromatic aldehydes with the fatty acids (p. 716), effected by heating with the chlorides of the acids, *e.g.*, $CH_3.COCl$ (Bertagnini), or with the free acids in the presence of zinc chloride or hydrochloric acid (Schiff):—

$$\underset{\text{Benzaldehyde.}}{C_6H_5.CHO} + \underset{\text{Acetic Acid.}}{CH_3.CO_2H} = \underset{\substack{\text{Cinnamic Acid,}\\ \text{Phenylacrylic Acid.}}}{C_6H_5.CH:CH.CO_2H} + H_2O;$$

or, better, with a mixture of the sodium salts and the anhydrides of the fatty acids (Perkin).

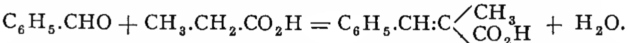
In the last case the reaction occurs between the aldehyde and the sodium salt (*Berichte*, 14, 2110: *Annalen*, 227, 48; compare *Berichte*, 19, Ref. 346), when, by the aldol condensation, we obtain a β-oxyacid:—

$$C_6H_5.CHO + CH_3.CO_2Na = \underset{\beta\text{-Phenylhydracrylic Acid.}}{C_6H_5.CH(OH).CH_2.CO_2Na},$$

which is then deprived of water by the acid anhydride:—

$$C_6H_5.CH(OH).CH_2.CO_2H = C_6H_5.CH{:}CH.CO_2H + H_2O.$$

All aromatic aldehydes (aldehyde phenols, aldehydic acids), react similarly with the homologous fatty acids and with many other compounds (p. 716). Thus, phenyl-crotonic acid, $C_6H_5.C_3H_4.CO_2H$, is produced from benzaldehyde by means of the sodium salt and the anhydride of propionic acid, and the coumaric acids, $C_6H_4(OH).C_2H_2.CO_2H$, etc., from the oxybenzaldehydes, $C_6H_4(OH).CHO$, with acetic acid. With the higher fatty acids the condensation occurs in such a manner that the two hydrogen atoms are withdrawn from the carbon atom in union with carboxyl (*Annalen*, 204, 187, and 208, 121):—



$$C_6H_5.CHO + \underset{\text{Propionic Acid.}}{CH_3.CH_2.CO_2H} = \underset{\text{Phenyl-meth-acrylic Acid.}}{C_6H_5.CH{:}C\begin{cases}CH_3\\CO_2H\end{cases}} + H_2O.$$

Similarly, phenyl-paraconic acid (p. 793), and (by withdrawal of CO_2) phenyl-isocrotonic acid (p. 813) are obtained from benzaldehyde with sodium succinate and acetic anhydride. Benzalmalonic acid, $C_6H_5.CH{:}C(CO_2H)_2$, and cinnamic acid are formed from benzaldehyde and malonic acid. Glacial acetic acid may be employed instead of acetic anhydride (*Berichte*, 16, 1436, 2516).

(2) By condensation of benzaldehydes with fatty acid esters, by means of sodium ethylate or metallic sodium; esters of the unsaturated acids are produced (Claisen) (p. 716) (*Berichte*, 23, 976):—

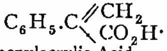
$$C_6H_5.CHO + CH_3.CO.O.C_2H_5 = C_6H_5.CH{:}CH.CO_2.C_2H_5 + H_2O.$$

1. Phenyl Acrylic Acids, $C_6H_5.C_2H_2.CO_2H$.

According to the structural theory, there are two possible isomerides, with this formula:—

(1) $C_6H_5.CH{:}CH.CO_2H$ and (2)

β-Phenylacrylic Acid.

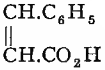


$$C_6H_5.C\begin{cases}CH_2\\CO_2H\end{cases}.$$

α-Phenylacrylic Acid.

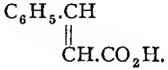
The first belongs to cinnamic acid; the second to atropic acid (p. 813). Cinnamic acid, in accordance with the stereochemical representations, can occur in two stereochemical forms (similar to crotonic acid (p. 238) and fumaric and maleïc acids (p. 425):—

(1)



$$\begin{array}{l}CH.C_6H_5\\\|\\CH.CO_2H\end{array}$$

(2)



$$\begin{array}{r}C_6H_5.CH\\\|\\CH.CO_2H.\end{array}$$

The first is the plane-symmetric arrangement; the second, the axially-symmetric or preferable configuration (p. 52). Wislicenus gives cinnamic acid the first formula. The formation of the acid by the reduction of phenyl-propiolic acid argues in favor of this view (*Berichte*, 22, 1181). However, there is the opposing fact that the recently discovered *isocinnamic acid* (p. 812), which must be given the axially-symmetric formula (2) is less stable than ordinary cinnamic acid and is readily converted into it. Furthermore, these stereochemical ideas have been proved insufficient by the discovery of a third β-phenylacrylic acid—*allo*-cinnamic acid (p. 813).

Cinnamic Acid, $C_9H_8O_2 = C_6H_5.CH:CH.CO_2H$, β-Phenylacrylic acid (*Acidum cinnamylicum*), occurs in Peru and Tolu balsams (p. 742), in storax and in some benzoïn resins. It results in the oxidation of its aldehyde or its alcohol, by the condensation of benzaldehyde with sodium acetate, by the decomposition of benzal malonic acid, and by the reduction of phenylpropiolic acid with zinc dust and glacial acetic acid (*Berichte*, 22, 1181).

Cinnamic acid is obtained either synthetically from benzaldehyde, or from storax (*Styrax officinalis*)—the pressed-out, thick sap of the bark of *Liquidambar orientale*. This contains, besides a resin, some free cinnamic acid and styrolene, C_8H_8, but chiefly *styracine* (cinnamic cinnamate and phenyl-propylic cinnamate p. 711). The styrolene is distilled off upon boiling with water. The residue is boiled with a soda solution, in order to remove the cinnamic acid; cold alcohol will extract the resin from what remains and only styracine is left. To obtain the cinnamic acid, storax is boiled for some time with sodium hydroxide, when the cinnamyl alcohol which is formed will distil over. Hydrochloric acid precipitates cinnamic acid from the solution. It is purified by distillation or crystallization from benzine (comp. *Annalen*, 188, 194).

To get the acid from benzaldehyde, a mixture of the latter (3 parts) with sodium acetate (3 parts) and acetic anhydride (10 parts), is boiled for several hours, water is then added and the acid dissolved in soda (*Berichte*, 10, 68). A more convenient procedure consists in heating benzalchloride, $C_6H_5.CHCl_2$ (1 part) with sodium or potassium acetate (2 parts) to 200°.

Cinnamic acid crystallizes from hot water in fine needles, from alcohol in thick prisms, is odorless, melts at 133°, and when quickly heated distils near 300° with almost no decomposition. It is soluble in 3500 parts of water of 17°, and readily in hot water.

The *cinnamates* are similar to the benzoates; ferric chloride produces a yellow precipitate in their solutions. In chemical character cinnamic acid closely resembles the acids of the acrylic acid series. Fusion with caustic potash decomposes it into benzoic and acetic acids (p. 236):—

$$C_6H_5.CH:CH.CO_2H + 2KOH = C_6H_5.CO_2K + CH_3.CO_2K + H_2.$$

Nitric acid and chromic acid oxidize it to benzaldehyde and benzoic acid. When heated with water to 180–200°, or with lime, it breaks up into CO_2 and styrolene. The acid of distyrene, $C_{17}H_{16}O_2$, and distyrolene are produced on heating with sulphuric acid.

The *ethyl ester* of cinnamic acid, $C_9H_7O_2(C_2H_5)$, is a liquid, boiling at 271°. It readily combines with bromine (dissolved in CS_2) to form the dibromide,

$C_9H_7Br_2O_2.C_2H_5$, melting at 69°. Like the esters of other unsaturated acids it combines with sodmalonic ester and sodacetoacetic ester (*Berichte*, **20**, Ref. 258, 504). The *methyl ester* melts at 33.5°, and boils at 263°. *Cinnameïn*, contained in Tolu and Peru balsams, consists of benzylic benzoate and cinnamate. It is obtained artificially by heating sodium cinnamate with benzylic chloride. It possesses an aromatic odor, crystallizes from alcohol in small, shining prisms, melting at 39°, and boiling about 320°.

Styracine, present in storax, is the cinnamic ester of cinnamyl alcohol, $C_8H_7.CO.O.C_9H_9$ (p. 808). It is best obtained from storax, by digesting the latter at 30° with dilute sodium hydroxide, until the residue (styracine) becomes colorless. It crystallizes from hot alcohol in fine needles, melting at 44°, and decomposes when distilled.

As cinnamic acid is unsaturated it is capable of taking two additional affinities. Hydrogen converts it into hydrocinnamic acid; chlorine produces dichlor-, bromine dibrom-hydrocinnamic acid (cinnamic dibromide), and hydrobromic and hydriodic acids convert it into β-brom- and iodo-hydro-cinnamic acids (p. 757). Hypochlorous acid changes it to phenyl-α-chlor-lactic acid (p. 776).

The halogen cinnamic acids (*o*-, *m*-, and *p*-), having the substitutions in the benzene nucleus, are obtained from the three diazocinnamic acids, $C_6H_4(N_2X).C_2H_2.CO_2H$, when they are digested with the haloid acids, and in this way all nine chlor-, brom-, and iodo-cinnamic acids, $C_6H_4X.C_2H_2.CO_2H$, have been prepared (*Berichte*, **15**, 2301, **16**, 2040).

Two possible isomerides can exist for each monohalogen cinnamic acid or phenylhaloid acrylic acid, with the substituting group in the side-chain:—

$$\underset{\alpha\text{-Chlor-cinnamic Acid.}}{C_6H_5.CH{:}CCl.CO_2H} \quad \text{and} \quad \underset{\beta\text{-Chlor-cinnamic Acid.}}{C_6H_5.CCl{:}CH.CO_2H.}$$

However, three (or four) isomeric chlor- and brom-cinnamic acids are known. We therefore have relations to deal with similar to those observed with fumaric and maleïc acids (p. 425). Apparently, the α- and β-acids possess the same structural formula (1), and the so-called β-acid bears the same relation to the α-acid that maleïc bears to fumaric acid. Following the suggestion of Michael we designate the β-chlor- and brom-acids, the allo-α-haloid cinnamic acids, and the two recently discovered chlor- and brom-cinnamic acids (γ and δ) are termed β- and allo-β-acid (*Berichte*, **20**, 550; **22**, Ref. 741). Erlenmeyer regards β-brom-cinnamic acid as corresponding to isocinnamic acid, as the latter is produced by the reduction of the former (*Berichte*, **23**, 3130). Until these relations are more fully determined the old designations α, β, etc., will be continued.

Two chlorcinnamic acids are obtained from αβ-dichlorhydrocinnamic acid by the action of alcoholic potash (*Berichte*, **15**, 788).

α-**Chlor-cinnamic Acid** is produced synthetically in the condensation of benzaldehyde and sodium chloracetate, when heated to 110°, with acetic anhydride (*Berichte*, **15**, 1945):—

$$C_6H_5.CHO + CH_2Cl.CO_2Na = C_6H_5.CH{:}CCl.CO_2Na + H_2O;$$

and from phenyl-α-chlorlactic acid (p. 776) by the withdrawal of water on heating with acetic anhydride (*Berichte*, 16, 854). It melts at 137°; its alkali salts are very readily soluble in water.

β-**Chlor-cinnamic Acid** melts at 111°; upon distillation it suffers a very slight transposition into the α-acid.

γ-and-δ **Chlor-cinnamic Acids** (β-and allo-β-acid) are produced by the addition of hydrogen chloride to phenyl-propiolic acid (p. 814). The first melts at 132°; the second at 142° (*Berichte*, 22, Ref. 741).

The brom-cinnamic acids are prepared like the chlor-cinnamic acids, by boiling the αβ-dibrom-hydro cinnamic acid with alcoholic potassium hydroxide. They can be separated by means of their ammonium salts, or by the fractional precipitation of the salt mixture (*Annalen*, 154, 146).

α-**Brom-cinnamic Acid**, the ammonium salt of which dissolves with difficulty, and is first precipitated, crystallizes from hot water in fine needles, melting at 131°, and then sublimes. Its *ethyl ester* boils at 290°. Concentrated sulphuric acid converts it into benzoyl acetic ester (*Berichte*, 19, 1392).

β-**Brom-cinnamic Acid** crystallizes from hot water in shining leaflets, melting at 121°. Its alkali salts are deliquescent. It changes to the α-acid if heated with hydriodic acid, and if distilled or heated for some time to 150–180°. It sustains a like transposition if converted into its ethers by alcohol and hydrochloric acid; the ester of the α-acid is then formed. Consult *Berichte*, 20, 551, 1386, upon the methyl and ethyl esters of α-and β-brom-cinnamic acids. Both acids yield phenyl-propiolic acid when boiled with alcoholic potassium hydroxide.

γ-**Brom-cinnamic Acid**, $C_6H_5.CBr:CH.CO_2H$(?) (see above), is produced by the addition of hydrobromic acid to phenyl-propiolic acid, $C_6H_5.C:C.CO_2H$ (*Berichte*, 19, 1936). A fourth acid is produced simultaneously; it is very similar to α-brom-cinnamic acid (*Berichte*, 20, 553). It dissolves with difficulty in cold alcohol, and crystallizes in needles, melting at 158.5° (153.5°).

The addition of two bromine atoms to phenyl-propiolic acid produces two αβ-dibrom-cinnamic acids, $C_6H_5.CBr:CBr.CO_2H$, called α- and β-. The α- melts at 139°, and the β- at 100°. The first passes readily into the second (*Annalen*, 247, 139).

Nitro-cinnamic Acids, $C_6H_4(NO_2).CH:CH.CO_2H$.

The introduction of cinnamic acid into nitric acid of specific gravity 1.5 leads to the formation of the ortho- (60 per cent.), and para-nitro acids, of which the former is the more easily soluble in hot alcohol. To separate them cover the acid mixture with 8–10 parts of absolute alcohol, and conduct hydrochloric acid gas rapidly into the liquid, until complete solution ensues. On cooling the para-ether separates. The mother liquor is evaporated, and the ortho-ether recrystallized from ether (*Annalen*, 212, 122, 150). The esters are saponified with sodium carbonate, or by heating with a mixture of 10 parts sulphuric acid, water and glacial acetic acid (equal parts), to 100°, or with water and sulphuric acid (*Annalen*, 221, 265).

The three isomeric acids can be prepared from the corresponding nitro-benzaldehydes by means of sodium acetate, etc.

o-**Nitro-cinnamic Acid** is insoluble in water, crystallizes from alcohol in needles, melting at 240°, and sublimes with partial decomposition. It colors concentrated sulphuric acid dark blue upon warming. Chromic acid oxidizes it to nitro-benzoic acid, and potassium permanganate converts it into *o*-nitrobenzaldehyde (p. 719). Bromine unites with it with difficulty, yielding the *di-*

bromide, $C_6H_4(NO_2).CHBr.CHBr.CO_2H$, melting at 180°, and forming *o*-nitrophenylpropiolic acid (p. 815), and then isatin when digested with sodium hydroxide. Indol results upon heating it with sodium hydroxide and zinc dust.

The *ethyl ester* of *o*-nitrocinnamic acid is very soluble in cold alcohol, crystallizes in needles or prisms, and melts at 44°. It yields carbostyril (p. 812), if digested with aqueous ammonium sulphide, and oxy-carbostyril if the solution be alcoholic. Tin and hydrochloric acid reduce it to *o*-amido-cinnamic ester (see below), and zinc dust and hydrochloric acid to hydrocarbostyril (p. 810). The ester readily unites with bromine, yielding the *dibromide*, $C_6H_4(NO_2).CHBr.CHBr.CO_2.C_2H_5$, melting at (110°) 71° (*Annalen*, **212**, 130), and serving for the preparation of *o*-nitrophenylpropiolic acid (p. 815).

m-**Nitro-cinnamic Acid** has been obtained from *m*-nitrobenzaldehyde, and consists of bright, yellow needles, melting at 197°. Oxidation changes it to *m*-nitrobenzoic acid; its ethyl ether melts at 79°.

p-**Nitro-cinnamic Acid** (see above) crystallizes from alcohol in shining prisms, and melts at 286°. Chromic acid oxidizes it to *p*-nitrobenzoic acid, while sulphuric and nitric acid convert it into *p*-nitrobenzaldehyde (p. 720). Its *ethyl ester* is almost insoluble in cold alcohol and ether, forms fine needles, and melts at 138°.

pa-**Dinitro-cinnamic Acid**, $C_6H_4(NO_2).CH:C(NO_2).CO_2H$, is obtained from *p*-nitrocinnamic acid by the action of sulphuric and nitric acids at —10°. It is very unstable, and at 0° decomposes into carbon dioxide and dinitrostyrolene (p. 801). Its *ethyl ester*, from *p*-nitrocinnamic ester, melts at 110°, and upon reduction yields *p*-amidophenyl alanine (p. 758). *m*-Nitrocinnamic acid deports itself very much like the *p*-acid (*Berichte*, **18**, Ref. 554).

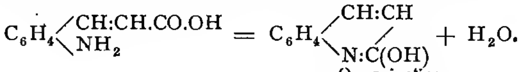
Amido-cinnamic Acids.

a **Amido-cinnamic Acid**, $C_6H_5.CH:C(NH_2).CO_2H$, obtained from benzoylamido-cinnamic acid (*Berichte*, **17**, 1620), is very similar to phenyl-alanine (p. 758), decomposes at 240° with formation of phenyl vinyl-amine, $C_6H_5.CH:CH(NH)_2$, and by reduction yields phenyl-alanine.

The amido-cinnamic acids, $C_6H_4(NH_2).C_2H_2.CO_2H$, with the substitutions in the benzene nucleus, can be obtained from the three nitro-cinnamic acids by reduction with tin and hydrochloric acid. There is greater advantage in reducing them with iron sulphate in alkaline solution (p. 592).

To prepare the *o*-amido-acid add an excess of ammonia and the ammoniacal solution of *o*-nitrocinnamic acid (5 grs.) to the boiling solution of green vitriol (50 grs.), continue boiling on a sand-bath and let the brownish-black precipitate of ferroso-ferric oxide subside. The solution should smell of ammonia, and be perfectly clear, and pure yellow in color, and if this be not the case add ammonia and apply heat. Concentrated hydrochloric acid is gradually added to the filtered solution of the ammonium salt of the amido-acid, as long as the yellow acid is precipitated (*Berichte*, **15**, 2294). For the reduction by means of ferrous sulphate and baryta water, see *Annalen*, **221**, 226.

o-**Amido-cinnamic Acid** separates in fine yellow needles, when hydrochloric acid is added to solutions of its salts. It melts at 158–159°, evolving gas. It is readily soluble in hot water, in alcohol and ether; the solutions exhibit a greenish-blue fluorescence. It yields ortho-coumaric acid when diazotized and boiled with water. The splitting-off of water causes it to pass into its lactime—the so-called carbostyril (α-oxyquinoline)—(p. 755):—



$$C_6H_4\Big\langle{CH:CH.CO.OH \atop NH_2} = C_6H_4\Big\langle{CH:CH \atop N:C(OH)} + H_2O.$$

α-Oxyquinoline.

This anhydride formation ensues on protracted boiling with hydrochloric acid, more rapidly on heating to 130° with hydrochloric acid, or upon heating the acetyl derivative of the *o*-amido-acid. When the acid is heated alone (unlike the *o*-amido-hydro-cinnamic acid, p. 757), it does not yield an anhydride (similar to ortho-coumaric acid).

The *ethyl ester* was first obtained by reducing *o*-nitro-cinnamic ester with tin and hydrochloric acid in alcoholic solution (*Berichte*, 15, 1422); a simpler method consists in conducting hydrochloric acid gas into the alcoholic solution of the free amido acid, evaporating and precipitating the aqueous solution with sodium acetate, when the ether will separate in fine yellow needles, melting at 77°. Its solutions show an intensely yellowish-green fluorescence. If digested at 90° with alcoholic $ZnCl_2$ it will yield ethyl-oxy-quinoline (see above); and oxy-quinoline if evaporated with hydrochloric acid.

Ethyl Amido-cinnamic Acid, $C_6H_4\Big\langle{CH:CH.CO_2H \atop NH.C_2H_5}$, is obtained when ethyl iodide and potassium hydroxide act upon *o*-amido-cinnamic acid. It melts at 125°, and forms a *nitroso*-body which, by reduction and the splitting-off of H_2O, yields an isindazole compound (p. 841).

The diazo-derivative of the amido-acid unites with sodium sulphite and forms *o*-**Hydrazine-cinnamic Acid**, $C_6H_4\Big\langle{C_2H_2.CO_2H \atop NH.NH_2}$, which on application of heat yields **Indazole**, $C_7H_6N_2$ (p. 841).

m- and *p*-**Amido-cinnamic Acids**, $C_6H_4.(NH_2).C_2H_2.CO_2H$, are similarly formed from *m*- and *p*-nitrocinnamic acids by reduction with green vitriol and ammonia (*Berichte*, 15, 2299); the first melts at 181°, the second at 176°. The halogen cinnamic acids (p. 809) result upon boiling the diazo-compounds with the haloid acids; and when water is employed *m*- and *p*-coumaric acids result.

2. **Isocinnamic Acid**, $C_6H_5.CH:CH.CO_2H$ (p. 807), is found in the acid mixture—truxillic, cinnamic and benzoic—that results upon decomposing cocaine (for the preparation of ecgonine). It is distinguished from the associated acids by greater fusibility and solubility (*Berichte*, 23, 141, 512). It is not present in the cinnamic acid obtained synthetically from oil of bitter almonds. It has been artificially prepared from β-bromcinnamic acid by replacing its bromine (*Berichte*, 23, 3131).

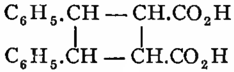
It is separated from the aqueous solution of its salts in the form of an oil, dissolves very easily in the common solvents, crystallizes from petroleum ether in brilliant crystals, melting at 45–47°, and when absolutely pure at 57°. It boils at 265°, changing at the same time to ordinary cinnamic acid, boiling at 300°.

It is also transformed into the latter by solution in sulphuric acid, or by boiling with iodine and carbon disulphide. A determination of its molecular weight by the method of Raoult leads to the simple molecular formula. The isocinnamic acid derivatives, the salts excepted, are mainly identical with those of ordinary cinnamic acid.

3. **Allo-cinnamic Acid,** $C_6H_5.CH:CH.CO_2H$, occurs with the iso-acid in the acid mixture in which the latter is present. It is not as soluble in ligroïne and melts at 68°. Its salts differ from those of the other two cinnamic acids. Potassium permanganate oxidizes the allo- and iso-cinnamic acids to benzaldehyde. Direct sunlight converts iso- and allo-cinnamic acids into ordinary cinnamic acid (*Berichte*, 23, 2510).

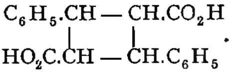
4. In addition to the three monomolecular cinnamic acids there are several (probably four)—

Dicinnamic Acids, $(C_9H_8O_2)_2$, or **Truxillic Acids.** They probably originate from tetramethylene, C_4H_8, and correspond to the formulas :—



$$\begin{array}{l} C_6H_5.CH - CH.CO_2H \\ \quad\;\; | \qquad\quad | \\ C_6H_5.CH - CH.CO_2H \end{array}$$

and



$$\begin{array}{l} C_6H_5.CH - CH.CO_2H \\ \qquad\;\; | \qquad\quad | \\ HO_2C.CH - CH.C_6H_5 \end{array}.$$

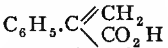
Their differences are based upon stereochemical isomerisms (*Berichte*, 23, 2516).

5. **Atropic Acid,** $C_9H_8O_2$, **α-Phenylacrylic Acid,** results from atropine, tropic acid and atrolactinic acid (p. 775) when they are heated with concentrated hydrochloric acid or with bartya water (*Annalen*, 195, 147). It crystallizes from hot water in monoclinic plates, is sparingly soluble in cold water, easily in ether, carbon disulphide and benzene; melts at 106°, and distils with aqueous vapor. Chromic acid oxidizes it to benzoic acid; sodium amalgam converts it into hydroatropic acid, and hydrochloric and hydrobromic acids change it to α- and β-halogen hydro atropic acids (p. 759).

Atropic acid sustains the same relation to cinnamic acid as hydro-atropic to hydro-cinnamic acid or methyl acrylic acid to ordinary crotonic acid (p. 238):—

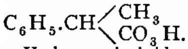
$C_6H_5.CH:CH.CO_2H$
Cinnamic Acid.

$C_6H_5.CH_2.CH_2.CO_2H$
Hydrocinnamic Acid.



$$C_6H_5.C\begin{cases} \!/\!\!/ CH_2 \\ \diagdown CO_2H \end{cases}$$

Atropic Acid.



$$C_6H_5.CH\begin{cases} \diagup CH_3 \\ \diagdown CO_3H. \end{cases}$$

Hydroatropic Acid.

Like all unsaturated acids when fused with caustic alkali, it splits at the point of double union, and yields formic and α-toluic acids, $C_6H_5.CH_2.CO_2H$, whereas cinnamic acid decomposes into benzoic and acetic acids.

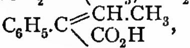
Protracted fusion, or heating with water or hydrochloric acid (in small quantity, even upon recrystallization), converts atropic acid into two polymeric *isatropic acids* $(C_9H_8O_2)_2$ (melting at 237° and 206°) which are very sparingly soluble, and no longer capable of yielding additive products.

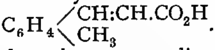
---

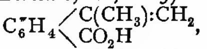
2. Acids, $C_{10}H_{10}O_2$.

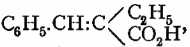
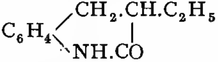
Phenyl-iso-crotonic Acid, $C_6H_5.CH:CH.CH_2.CO_2H$, is produced on heating benzaldehyde with sodium isosuccinate. Phenyl-paraconic acid (p. 793) is produced at first, but this then parts with carbon dioxide. The acid melts at 86°, and when boiled yields water and α-naphthol. It unites with hydrogen bromide, forming phenyl-γ-brombutyric acid, which yields phenyl-butyro-lactone (p. 777) with a soda solution. Boiling dilute sulphuric (1 part : 2 parts water) converts it directly into phenylbutyrolactone (p. 352).

Phenyl-methacrylic Acid,  $C_6H_5.CH{:}C\begin{cases}CH_3\\CO_2H\end{cases}$, is obtained from benzaldehyde and sodium propionate, as well as by the action of sodium upon propionic benzyl ester (*Berichte* 20, 617). It crystallizes from water in long needles, that melt at 78°, and boil at 288° Sodium amalgam converts it into phenylisobutyric acid. Bromine in the presence of alkali converts the amide of the latter into phenylisopropylamine, $C_6H_5.CH_2.CH(CH_3).NH_2$ (p. 160) (*Berichte*, 20, 618).

Methyl Atropic Acid,  $C_6H_5.C\begin{cases}CH.CH_3\\CO_2H\end{cases}$, is obtained from phenyl-acetic acid, $C_6H_5.CH_2.CO_2H$, and acetaldehyde. It melts at 135°.

Methyl Cinnamic Acids,  $C_6H_4\begin{cases}CH{:}CH.CO_2H\\CH_3\end{cases}$. The three isomerides, *o*-, *m*- and *p*-, have been prepared from the corresponding toluic aldehydes by means of sodium acetate. The *ortho* melts at 169°; the *para* at 197° (*Berichte*, 23, 1029, 1033) and the *meta* at 107° (*Berichte*, 20, 1215).

Propenyl Benzoic Acid,  $C_6H_4\begin{cases}C(CH_3){:}CH_2\\CO_2H\end{cases}$, is obtained from oxyisopropyl benzoic acid (p. 777). Boiling hydrochloric acid converts it (analogous to atropic acid) into a polymeric acid.

3. **Phenyl-angelic Acid,** $C_{11}H_{12}O_2 =$  $C_6H_5.CH{:}C\begin{cases}C_2H_5\\CO_2H\end{cases}$, from benzaldehyde and normal butyric acid, yields **Phenyl-valeric Acid,** $C_6H_5.CH_2.CH(C_2H_5).CO_2H$, with sodium amalgam. It melts at 104°. The ortho-nitro product of this is reduced to an ortho-amido-acid, which parts with water and yields the anhydride, **ethyl-hydrocarbostyril,** $C_{11}H_{13}NO =$  $C_6H_4\begin{cases}CH_2.CH.C_2H_5\\NH.CO\end{cases}$, which can be easily changed into β-ethyl-quinoline, $C_9H_6(C_2H_5)N$ (analogous to the formation of quinoline from ortho-amido-hydrocinnamic acid, p. 758).

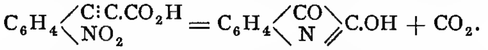
***p*-Cumenyl-Acrylic Acid,** $C_{12}H_{14}O_2 = C_3H_7.C_6H_4.CH{:}CH.CO_2H$ (with isopropyl), may be obtained from cumic aldehyde and sodium acetate. It melts at 158°. Nitration produces *p*-nitrocinnamic acid and *o*-nitrocumenyl-acrylic acid (melting at 156°). Cumin indigo (di-isopropyl indigo) can be obtained from the latter (this is analogous to the rearrangement of *o*-nitro-cinnamic acid). *o*-Amido-cumenyl-acrylic acid, obtained by reduction, condenses to cumostyril (isopropyl-carbostyril) (p. 812), and cumoquinoline. In addition to *o*-nitro-cumenyl-acrylic acid, *o*-nitro *p*-propylcinnamic acid, $C_3H_7.C_6H_3(NO_2)CH{:}CH.CO_2H$ (with the normal propyl group), is also formed by a molecular rearrangement. Its amido-derivative is *n*-propylcarbostyril (*Berichte*, 19, 255; 20, 2771).

We have an example of a doubly unsaturated acid in

Phenyl-propiolic Acid, $C_9H_6O_2 = C_6H_5.C{\vdots}C.CO_2H$ (p. 244). It is obtained by boiling α- and β-brom-cinnamic acids with alcoholic potash, by acting upon sodium phenyl-acetylene, $C_6H_5.C{\vdots}CNa$, with carbon dioxide, and when the latter and sodium act upon β-brom-styrolene. It is prepared by boiling the dibromide of ethyl cinnamate (p. 809), with alcoholic potash (3 molecules). It crystallizes from hot water or carbon disulphide in long, shining needles, melting at 136–137° and subliming; under water it melts at 80°. When heated to 100° with water it decomposes into carbon dioxide and phenyl acetylene. It combines with 2 and 4Br, and yields hydrocinnamic acid with sodium amalgam. Zinc dust and glacial acetic acid, or sodium and methyl alcohol, convert it into cinnamic acid. When its ethyl ester is dissolved in sulphuric acid and diluted with water we get benzoyl acetic ester (p. 763).

Nitro-phenyl propiolic acids, $C_6H_4(NO_2).C{:}C.CO_2H$.

o-**Nitro-phenyl Propiolic Acid** is obtained when aqueous soda acts upon the dibromide of *o*-nitro-cinnamic acid. An easier method consists in mixing the dibromide of the *o*-nitro-cinnamic acid ester (p. 811) with alcoholic potash (3 molecules) (*Annalen*, 212, 140). It occurs in commerce in the form of a 25 per cent. paste. To purify this it is first converted into the ethyl ester. The acid crystallizes from hot water or alcohol, in needles, or shining leaflets, and decomposes at 156°. When boiled with water it decomposes into carbon dioxide and *o*-nitrophenyl acetylene (p. 802). When boiled with alkalies it yields isatin:—



$$C_6H_4\left\langle\begin{matrix}C{:}C.CO_2H\\ NO_2\end{matrix}\right. = C_6H_4\left\langle\begin{matrix}CO\\ N\end{matrix}\right\rangle C.OH + CO_2.$$

It dissolves in concentrated sulphuric acid, with conversion into the isomeric *isatogenic acid*, which at once forms carbon dioxide and isatin.

If digested with alkaline reducing agents (grape sugar and potassium hydroxide, ferrous sulphate, hydrogen sulphide, potassium xanthate) *it readily changes to indigo blue* (Baeyer, 1880):—

$$2C_9H_5NO_4 + 2H_2 = C_{16}H_{10}N_2O_2 + 2CO_2 + 2H_2O.$$

Therefore nitrophenyl propiolic acid may serve as a substitute for natural indigo, especially in calico printing.

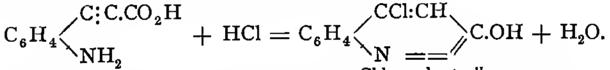
The *ethyl ester* of the acid is obtained by rapidly conducting hydrochloric acid gas into the mixture of the acid and 10 parts absolute alcohol, until solution ensues. It is very soluble in ether and separates in large crystals, melting at 60–61°. It is saponified on heating a mixture of sulphuric acid, water and glacial acetic acid (equal parts) to 100°. (p. 810) When it is dissolved in sulphuric acid it changes to the isomeric isatogenic ester. Ammonium sulphide reduces it to the indoxylic ester.

p-Nitrophenyl Propiolic Acid is formed from the *p*-nitro cinnamic ester, after the same manner as the ortho-acid (*Annalen* 212, 139, 150). It crystallizes from hot alcohol in needles, and melts at 198° (181°) with decomposition. When boiled with water it breaks up into carbon dioxide and *p*-nitrophenyl acetylene. It yields *p*-nitroacetophenone (p. 728), if digested at 100° with sulphuric acid.

The *ethyl ester* crystallizes from alcohol in needles; melting at 126°. When digested with sulphuric acid at 35° it forms *p*-nitrobenzoyl acetic acid (p. 763).

o **Amido-phenyl Propiolic Acid** is obtained by reducing nitrophenyl propiolic acid with ferrous sulphate and ammonia (*Berichte*, 16, 679). It separates as a yellow, crystalline powder, melting at 128–130°, with decomposition into carbon dioxide and amidophenyl acetylene (p. 802). When boiled with water it yields amido-acetophenone (p. 728).

γ-Chlorcarbostyril results when the acid is boiled with hydrochloric acid, and γ-oxycarbostyril upon heating it with sulphuric acid. Here there occurs a closed, ringed-shaped union of atoms (*Berichte*, 15, 2147):—



$$C_6H_4\left<\begin{matrix}C{:}C.CO_2H\\NH_2\end{matrix}\right. + HCl = C_6H_4\left<\begin{matrix}CCl{:}CH\\N==\end{matrix}\right>C.OH + H_2O.$$

γ-Chlorcarbostyril.

Sodium nitrite converts the hydrochloride into the diazo-chloride, which at 70° yields cinnoline-oxy-carboxylic acid (see this).

Homologous Acids with *two double unions*:—

Cinnamenyl Acrylic Acid, $C_{11}H_{10}O_2 = C_6H_5.CH{:}CH.CH{:}CH.CO_2H$, *Cinnamenyl Methacrylic Acid*, $C_{12}H_{12}O_2 = C_6H_5.CH{:}CH.CH{:}C\left<\begin{matrix}CH_3\\CO_2H\end{matrix}\right.$, etc., have been produced by the condensation of cinnamyl aldehyde with acetic acid, propionic acid, etc. (p. 806).

Ketonic Acids (p. 761).

Cinnamyl Formic Acid, $C_6H_5.CH{:}CH.CO.CO_2H$. This is the only unsaturated α-ketonic acid known. It is obtained, like benzoyl formic acid, from cinnamic chloride, with potassium cyanide, etc.; and by the condensation of benzaldehyde and pyroracemic acid, $CH_3.CO.CO_2H$, by means of hydrochloric acid gas (p. 716). It is a gummy mass and is gradually decomposed into its components by the alkalies, even in the cold.

The *ortho-nitro derivative* is similarly formed from *o*-nitrobenzaldehyde, melts at 135°, and is changed by alkalies, even in the cold, with elimination of oxalic acid, into indigo (*Berichte*, 15, 2863):—

$$2C_6H_4(NO_2).C_2H_2.CO.CO_2H + 2H_2O = \underset{\text{Indigo.}}{(C_6H_4{:}C_2ONH)_2} + 2C_2O_4H_2 + 2H_2O.$$

Unsaturated *β-ketonic acids* are produced by the condensation of benzenes with maleïc anhydride, etc., by means of $AlCl_3$ (see benzoyl propionic acid) (just as phthalic anhydride condenses with fatty acids and benzenes p. 787):—

$$C_6H_6 + C_2H_2(CO)_2O = C_6H_6.CO.C_2H_2.CO_2H.$$

Benzoyl Acrylic Acid, $C_6H_5.CO.CH{:}CH.CO_2H$, from benzene and maleïc anhydride, crystallizes with water in shining leaflets, melting at 64°, but at 97° when anhydrous (*Berichte*, 15, 889). It yields benzoyl propionic acid by reduction (p. 764).

Benzoyl Crotonic Acid, $C_6H_5.CO.C_3H_4.CO_2H$, from benzene and citraconic anhydride, melts at 113°.

Benzal-Aceto-acetic Acid, $C_6H_5.CH{:}C\left<\begin{matrix}CO.CH_3\\CO_2H\end{matrix}\right.$. Its *ethyl ester* is formed by the condensation of benzaldehyde and aceto-acetic ester by means of HCl or $ZnCl_2$. Sometimes it solidifies in crystalline form, and melts at 60°; it boils near 296°. It condenses with phenylhydrazine to diphenylmethylpyrazole. Benzaldehyde condenses with ethyl and diethyl aceto-acetic esters, acting at the time upon the methyl group (*Annalen*, 218, 181).

β-**Benzal-lævulinic Acid**, $C_6H_6.CH{:}C\left<\begin{matrix}CO.CH_3\\CH_2.CO_2H\end{matrix}\right.$, is produced by the condensation of benzaldehyde and lævulinic acid in acid solution, and melts at 125°. It parts with water upon distillation and forms aceto α naphthol, $C_6H_4{:}C_4H_2(OH).(CO.CH_3)$, just as α-naphthol is produced from phenyl-isocrotonic acid (p. 813).

When benzaldehyde and lævulinic acid condense in alkaline solution the product is:—

δ-**Benzal-lævulinic Acid**, $C_6H_5CH{:}CH.CO.C_2H_4.CO_2H$, melting at 120° (*Berichte*, 23, Ref. 576).

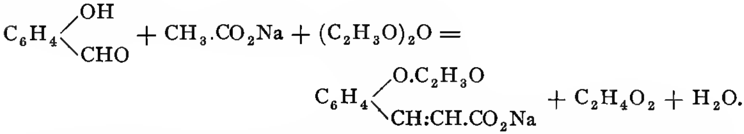
Oxy-acids and coumarins.

The unsaturated oxy-acids, or phenol acids, containing hydroxyl in the benzene nucleus can be obtained from the unsaturated amido-acids (the amido-cinnamic acids) by boiling the diazo-derivatives with water:—

$$C_6H_4\left<\begin{matrix}NH_2\\CH{:}CH.CO_2H\end{matrix}\right. \quad \text{yields} \quad C_6H_4\left<\begin{matrix}OH\\CH{:}CH.CO_2H.\end{matrix}\right.$$

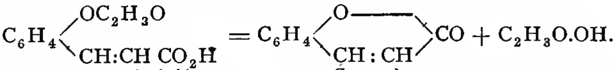
Amido-cinnamic Acid. Oxy-cinnamic Acid.

They are synthetically prepared from the oxybenzaldehydes, $C_6H_4(OH).CHO$, by heating them with the sodium salts of the fatty acids (p. 806). The acidyl derivatives of the oxy-acids are first produced:—



$$C_6H_4\left<\begin{matrix}OH\\CHO\end{matrix}\right. + CH_3.CO_2Na + (C_2H_3O)_2O = C_6H_4\left<\begin{matrix}O.C_2H_3O\\CH{:}CH.CO_2Na\end{matrix}\right. + C_2H_4O_2 + H_2O.$$

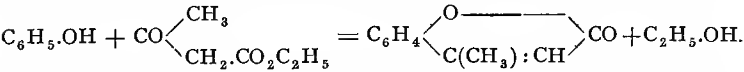
These yield the acids when saponified with alkalies. Those isomerides, belonging to the ortho-series, can here, by exit of water, yield inner anhydrides (δ-lactones), called *coumarins*:—



$$C_6H_4\left<\begin{matrix}OC_2H_3O\\CH{:}CH\ CO_2H\end{matrix}\right. = C_6H_4\left<\begin{matrix}O\text{———}\\CH : CH\end{matrix}\right>CO + C_2H_3O.OH.$$

Aceto-*o*-coumaric Acid. Coumarin.

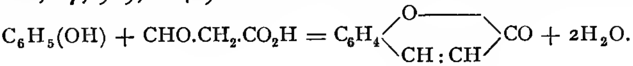
Such coumarins are produced (1) by the condensation of phenols and aceto-acetic esters when they are heated with sulphuric acid (v. Pechmann, *Berichte*, 16, 2126):—



$$C_6H_5.OH + CO\left<\begin{matrix}CH_3\\CH_2.CO_2C_2H_5\end{matrix}\right. = C_6H_4\left<\begin{matrix}O\text{————}\\C(CH_3) : CH\end{matrix}\right>CO + C_2H_5.OH.$$

Resorcinol especially is very reactive, forming β-methyl umbelliferon. Orcin yields dimethyl umbelliferon, and pyrogallol yields methyl daphnetin, etc. (*Berichte*, 17, 2129, 2187). Citric acid (*Berichte*, 17, 931) reacts like aceto-acetic ester. Resorcinol and phloroglucin also yield di- and tri-coumarins (*Berichte*, **20**, 1329).

2. The condensation of the phenols with malic acid when heated with sulphuric acid or $ZnCl_2$ (it is very probable the malic acid first yields malonic aldehyde, $CHO.CH_2.CO_2H$) (v. Pechmann, *Berichte*, **17**, 929, 1646):—



$$C_6H_5(OH) + CHO.CH_2.CO_2H = C_6H_4\left\langle\begin{array}{l}O\text{———}\\CH:CH\end{array}\right\rangle CO + 2H_2O.$$

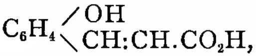
Coumarin.

Resorcinol yields umbelliferon (oxycoumarin, p. 821), while daphnetin is obtained from pyrogallol (p. 823). Hydroquinone, orcin, phloroglucin and β-naphthol react similarly.

3. Dicoumarins are produced by the condensation of salicylic aldehyde and succinic acid (p. 807); with pyrotartaric acid the product is coumarin propionic acid (*Berichte*, 23, Ref. 97).

The coumarins correspond to the δ-lactones of the paraffin series, derived from the δ-oxy-acids (p. 353). They are distinguished from them by their much greater stability. Boiling water does not affect them; they dissolve unaltered in the alkalies (carbon dioxide again separates them) and are converted into salts of the *o*-oxy-acids by protracted heating with concentrated alkalies. Similarly, the oxy-acids are not converted into the corresponding coumarins either by boiling with water, or by heating them. This change only occurs upon distilling their aceto-compounds, or through the action of hydrobromic acid (*Berichte*, **18**, Ref. 28).

(1) Oxycinnamic Acids, $C_6H_4\left\langle\begin{array}{l}OH\\CH:CH.CO_2H,\end{array}\right.$ Coumaric Acids.



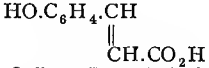
Meta-coumaric Acid (1, 3), from *m*-amido-cinnamic acid and from *m*-oxybenzaldehyde (p. 817), crystallizes from hot water in white prisms, and melts at 191°. Sodium amalgam converts it into hydro-*m*-coumaric acid (p. 774).

Para-coumaric Acid (1, 4) is obtained from *p*-amido-cinnamic acid, and from *p*-oxybenzaldehyde, also on boiling the extract of aloes with sulphuric acid. Preparation, *Berichte*, 20, 2528. It crystallizes from hot water in needles, and melts at 206°. Sodium amalgam converts it into hydropara-coumaric acid; fused with KOH it yields *p*-oxybenzoic acid and acetic acid. It is identical with *naringinic acid* from the glucoside naringine (*Berichte*, **20**, 296).

Ortho-coumaric Acid (1, 2) occurs in *Melilotus officinalis*, together with *o*-hydro-coumaric acid. Nitrous acid converts *o*-amido-cinnamic acid into coumaric acid; its acetyl derivative is obtained from salicylic aldehyde and sodium acetate. It is most readily prepared by boiling coumarin for some time with concentrated potassium hydroxide, or better, with sodium ethylate (*Berichte*, 18, Ref. 28; 23, 1714).

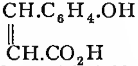
Ortho-coumaric acid is very easily soluble in hot water and in alcohol, and melts with decomposition at 208°. Sodium amalgam converts it into melilotic acid, and fusion with potassium hydroxide into salicylic and acetic acids. Its alkali salt solutions are yellow colored and show a green fluorescence. *Aceto-coumaric acid* (see above) melts at 146°, and is split into acetic acid and coumarin on the application of heat. The free coumaric acid heated alone does not yield coumarin, but only when treated with acetic chloride or anhydride.

In addition to the above ortho-coumaric acid (β) we have also α-coumaric acid or the so-called **Coumarinic Acid**, $C_6H_4\left\langle\begin{matrix}OH\\C_2H_2.CO_2H\end{matrix}\right.$, which is known only in its salts and ethers, and when set free at once yields water, and its anhydride—coumarin. Its relations to common coumaric acid are perfectly similar to those of maleïc to fumaric acid; the latter, according to Wislicenus, is *axially-symmetric*, whereas coumarinic acid, only known in its anhydride, is *plane-symmetric*:—



$$\begin{matrix}HO.C_6H_4.CH\\ \quad\quad\quad\quad \|\\ \quad\quad\quad\quad CH.CO_2H\end{matrix}$$

Ordinary Coumaric Acid.



$$\begin{matrix}CH.C_6H_4.OH\\ \|\\ CH.CO_2H\end{matrix}$$

Coumarinic Acid.

These assumptions do not accord with the behavior of nitrocoumaric ester, which rather points to the idea of Michael, that coumarinic acid is a dioxylactone (*Berichte*, 22, 1714). The basic salts of the acid, *e.g.*, $C_6H_4(ONa).C_2H_2.CO_2Na$, are obtained on boiling coumarin with dilute alkalies, and differ from the salts of ordinary coumaric acid, which are prepared by strongly heating coumarin with alkalies (see above). From the former acids precipitate coumarin, from the latter, coumaric acid. If coumarin be boiled with caustic potash (2 molecules) and methyl iodide (2 molecules), in alcoholic solution, we obtain a dimethyl ether, which, on saponification, yields **Methylcoumarinic Acid**, $C_6H_4(O.CH_3).C_2H_2.CO_2H$, melting at 90°; greater heat (150°) produces a dimethyl ether which when saponified, yields **Methylcoumaric Acid**, melting at 182°. The latter acid is more readily obtained by boiling coumaric acid with caustic potash (1 molecule), methyl iodide and alcohol. It is, moreover, directly prepared from methyl salicylic aldehyde, $C_6H_4(O.CH_3).CHO$ (p. 817), by means of sodium acetate, etc. Strong heat, boiling with hydrochloric acid and even sunlight, converts methyl coumarinic acid into stable methyl coumaric acid. Sodium amalgam converts both acids into methyl-melilotic acid; and also yields the same addition product with bromine. Potassium permanganate oxidizes both to methyl salicylic acid. **Ethyl coumarinic** and **Ethyl coumaric Acid**, $C_6H_4(O.C_2H_5).C_2H_2.CO_2H$, manifest the same deportment; the former melting at 102°, the latter at 132° (*Annalen*, 216, 139).

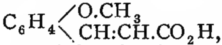
Coumarin, $C_9H_6O_2 = C_6H_4\left\langle\begin{matrix}O\\C_2H_2\end{matrix}\right\rangle CO$, the δ-lactone of coumarinic acid, occurs in *Asperula odorata*, in the Tonka beans (from *Dipterix odorata*), and in *Melilotus officinalis*. It is artificially prepared by heating salicylic aldehyde with sodium acetate and acetic anhydride. At first we get aceto-coumaric acid, which decomposes further into acetic acid and coumarin (p. 818). It is soluble in hot water, readily in alcohol and ether, crystallizes in shining prisms, possesses the odor of the *Asperula,* melts at 67°, and distils at 290°. When warmed it dissolves in alkalies with a yellow color; on boiling coumarinic and coumaric acids result (see above). Potassium permanganate destroys it (like the homologous phenols). Sodium amalgam changes it to melilotic acid (p. 774).

Bromine converts it into a *dibromide,* $C_9H_6Br_2O_2$, melting at 105°. Coumarilic acid is produced when coumarin dibromide or brom-coumarin is boiled with alcoholic potash (p. 825).

o-**Nitro-coumarin,** $C_9H_5(NO_2)O_2$, from *o* nitrosalicylic aldehyde, melts at 191°, and cannot be directly rearranged into carbostyril (*Berichte,* **22,** 1705). *o*-Nitro-carbostyril is produced by heating the amide of *o*-nitro coumarinic acid with hydrochloric acid.

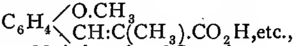
When salicylic aldehyde acts upon the higher fatty acids we derive homologous alkyl coumarins (p. 807) **Propionyl-coumarin,** $C_{10}H_8O_2$, α-methyl coumarin, from propionic acid, melts at 90°, and boils at 292°. *β-Methyl coumarin* (p. 818), from phenol and acetoacetic ester, melts at 125°. **Butyryl-Coumarin,** $C_{11}H_{10}O_2$, α-ethyl coumarin, from butyric acid, and salicylaldehyde melts at 71°, and boils at 299°.

The alkyl-ether acids,



$C_6H_4<\begin{matrix}O.CH_3\\CH:CH.CO_2H,\end{matrix}$

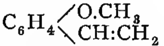
Methyloxyphenyl Acrylic Acid.



$C_6H_4<\begin{matrix}O.CH_3\\CH:C(CH_3).CO_2H,\end{matrix}$ etc.,

Methyloxyphenyl Crotonic Acid.

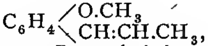
derived from the alkyl-oxy-benzaldehydes (methyl salicylic aldehyde, methyl anisaldehyde), yield esters of unsaturated phenols (just as styrolene arises from cinnamic acid) by the action of hydrochloric acid and a soda solution, when carbon dioxide is eliminated, *e. g.*:—



$C_6H_4<\begin{matrix}O.CH_3\\CH:CH_2\end{matrix}$

Vinylanisol.

and



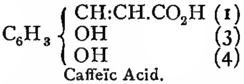
$C_6H_4<\begin{matrix}O.CH_3\\CH:CH.CH_3,\end{matrix}$ etc.

Propenylanisol.

The latter is the *anethol* (p. 803) found in anise oil.

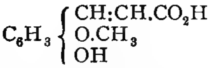
Dioxyacids.

The dioxyphenyl acrylic acids are *caffeïc* acid and its methyl esters: *ferulic* and *isoferulic acids,* and *umbellic acid,* whose anhydride is *umbelliferon.* The first acids are intimately related to protocatechuic acid and its ethers, and to vanillic and iso-vanillic acids, since they have the side groups in the same position (p. 780):—



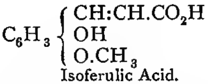
$C_6H_3\left\{\begin{matrix}CH:CH.CO_2H & (1)\\OH & (3)\\OH & (4)\end{matrix}\right.$

Caffeïc Acid.



$C_6H_3\left\{\begin{matrix}CH:CH.CO_2H\\O.CH_3\\OH\end{matrix}\right.$

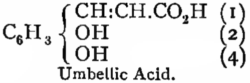
Ferulic Acid.



$C_6H_3\left\{\begin{matrix}CH:CH.CO_2H\\OH\\O.CH_3\end{matrix}\right.$

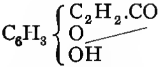
Isoferulic Acid.

In umbellic acid the side-chains occupy the same position as in β-resorcylic acid (p. 778); one hydroxyl group is in the ortho-place referred to the side-chain containing carbon, hence the acid can yield an inner anhydride (umbelliferon), just as *o*-coumaric acid forms coumarin:—



$$C_6H_3\begin{cases}CH{:}CH.CO_2H & (1)\\ OH & (2)\\ OH & (4)\end{cases}$$

Umbellic Acid.



$$C_6H_3\begin{cases}C_2H_2.CO\\ O\\ OH\end{cases}$$

Umbelliferon.

Caffeïc Acid, $C_9H_8O_4$, is obtained when the tannin of coffee (p. 785) is boiled with potassium hydroxide. It is prepared artificially from proto-catechuic aldehyde if the latter be heated with acetic anhydride and sodium acetate, and then the resulting diacetate saponified. It crystallizes in yellow prisms, and is very readily soluble in hot water and alcohol. The aqueous solution reduces silver solutions upon application of heat, but not alkaline cupric solutions. Ferric chloride causes a green coloration, which becomes dark red by the addition of soda. When fused with potassium hydroxide, caffeïc acid decomposes into protocatechuic acid and acetic acid. Pyrocatechin results when it is exposed to dry distillation. Sodium amalgam converts it into hydrocaffeïc acid (p. 782).

Ferulic Acid, $C_{10}H_{10}O_4$, is the methyl-phenol ether of caffeïc acid and corresponds to vanillin. It is found in asafœtida, from which it may be obtained by precipitation with lead acetate and by the subsequent decomposition of the lead salt with sulphuric acid. It has been synthetically prepared from vanillin when heated with sodium acetate, etc.; also from *m*-methoxy-cinnamic ester (from *m*-nitrobenzaldehyde) (*Berichte*, 18, Ref. 682). It is very soluble in hot water, crystallizes in shining needles or prisms, and melts at 169°. Ferric chloride imparts a yellowish-brown coloration to its aqueous solution. When fused with potassium hydroxide, it forms protocatechuic acid and acetic acid. Potassium permanganate oxidizes the acetate to aceto-vanillin. Ferulaldehyde, the aldehyde of ferulic acid, has been obtained from glycovanillin (*Berichte*, 18, 3482).

Isoferulic Acid, Hesperetinic Acid, $C_{10}H_{10}O_4$ (see above), was first obtained from the glucoside hesperidine, and is prepared by partially methylating caffeïc acid (together with a little ferulic acid). It melts at 228°, and if fused with potassium hydroxide decomposes into protocatechuic acid and acetic acid. The oxidation of its acetate produces isovanillic acid; sodium amalgam yields isohydroferulic acid (p. 782).

By the introduction of more methyl into ferulic and isoferulic acids, as well as caffeïc acid, there results dimethyl caffeïc acid, $C_6H_3(O.CH_3)_2.C_2H_2.CO_2H$, melting at 181°; this is oxidized by potassium permanganate to dimethyl protocatechuic acid. *Methylene Caffeïc Acid*, $C_6H_3\left(\begin{matrix}O\\O\end{matrix}\!>\!CH_2\right).C_2H_2.CO_2H$, is obtained synthetically from piperonal (p. 726) by means of sodium acetate, etc.

Umbellic Acid, $C_9H_8O_4 = C_6H_3(OH)_2.C_2H_2.CO_2H$ (see above), is obtained by digesting umbelliferon with caustic potash, and then precipitating with acids. It is a yellow powder, decomposing about 240°. Its anhydride, corresponding to coumarin, is—

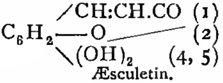
Umbelliferon, $C_9H_6O_3$, Oxycoumarin. It is found in the bark of *Daphne mezereum*, and is obtained by distilling different resins, such as galbanum and asafœtida. It is obtained synthetically from β-resorcyl aldehyde, $C_6H_3(OH)_2.CHO$, by means of sodium acetate, etc.; and also by the condensation of resorcinol with malic acid (p. 818). It consists of fine needles, sparingly soluble in hot water and ether, melts at 224°, and sublimes undecomposed. When heated it has an odor resembling that of coumarin. It dissolves with a beautiful blue fluorescence, in concentrated sulphuric acid. It dissolves in cold alkaline hydroxides unaltered, but when heated umbellic acid is produced. Sodium amalgam converts it into hydro-umbellic acid (p. 782). Fusion with caustic alkali affords β-resorcylic acid and resorcinol.

When umbelliferon is treated with methyl iodide and caustic alkali it conducts itself like coumarin (p. 819). The products of the reaction are α-**Dimethyl-umbellic Acid**, and the more stable β-**Dimethyl-umbellic Acid**, $C_6H_3(O.CH_3)_2.C_2H_2.CO_2H$; these correspond to methyl coumarinic and methyl coumaric acids (*Berichte*, 16, 2115; 19, 1777). Oxycoumarilic acid is formed in like manner from the dibromide by the action of alcoholic potash.

The so-called β-**Methyl-umbelliferon**, $C_6H_3(OH)\overset{O\overline{\qquad\qquad\qquad}}{\diagdown C(CH_3):CH\diagup}CO$, has been prepared synthetically by the condensation of resorcinol with aceto acetic esters (p. 818). It melts at 185°, and when fused with caustic potash yields resacetophenone, $C_6H_3(OH)_2.CO.CH_3$ (p. 729) and resorcinol (*Berichte*, 16, 2120). The introduction of methyl produces dimethyl β-methyl umbellic acid, $C_6H_3(O.CH_3)_2.C(CH_3):CH.CO_2H$, which potassium permanganate oxidizes to dimethyl-β-resorcylic acid (p. 778).

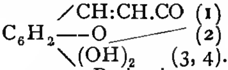
As a representative of the doubly unsaturated dioxyacid class we may mention **Piperic Acid**, $C_{12}H_{10}O_4 = C_6H_3\left(\genfrac{}{}{0pt}{}{O}{O}\!>CH_2\right).CH:CH.CH:CH.CO_2H$. Its side-chains are arranged like those in protocatechuic acid. Its potassium salt is produced when the alkaloid piperine is boiled with alcoholic potassium hydroxide. It consists of shining prisms. The free acid is almost insoluble in water, and crystallizes from alcohol in long needles, melting at 217°. Its salts with 1 equivalent of base are very sparingly soluble. It combines with four atoms of bromine. It is oxidized to piperonal when digested with potassium permanganate; at 0° the side-chain is eliminated as racemic acid (*Berichte*, 23, 2372). When fused with potassium hydroxide it breaks down into acetic, oxalic and protocatechuic acids. Chromic acid destroys it completely. Sodium amalgam converts it into two isomeric **hydropiperic acids**, $C_{12}H_{12}O_4$, α and β. The α-acid melts at 78°, and when digested with sodium hydroxide is converted into the β-acid, melting at 131°. The α-acid yields a dibromide with bromine; the β-acid when acted upon with sodium amalgam passes into the so-called **piperhydronic acid**, $C_{12}H_{14}O_4$, melting at 96°.

Æsculetin and *Daphnetin* are anhydrides (δ-lactones) of unsaturated trioxy-acids, and may also be designated dioxy-coumarins:—



$$C_6H_2\begin{cases}CH:CH.CO & (1)\\ O & (2)\\ (OH)_2 & (4,5)\end{cases}$$

Æsculetin.



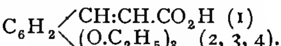
$$C_6H_2\begin{cases}CH:CH.CO & (1)\\ O & (2)\\ (OH)_2 & (3,4).\end{cases}$$

Daphnetin.

The three hydroxyls in æsculetin have the same position as in oxyhydroquinone, $C_6H_3(OH)_3$ (1, 3, 4), and in daphnetin they are in the same relation as in pyrogallol. Their corresponding acids are only known as tri-ethyl-ether acids:—

$$C_6H_2\begin{cases}CH:CH.CO_2H & (1)\\ (O.C_2H_5)_3 & (2,4,5)\end{cases}$$

Triethyl-æsculetinic acid.



$$C_6H_2\begin{cases}CH:CH.CO_2H & (1)\\ (O.C_2H_5)_3 & (2,3,4).\end{cases}$$

Triethyl Daphnetic acid.

Æsculetin, $C_9H_6O_4$, is present in the bark of the horse chestnut, partly free and partly as the glucoside *æsculin*, from which it is prepared by decomposition with acids or ferments. It crystallizes with a molecule of water in fine needles or leaflets, and dissolves with a yellow color in the alkalies. It reduces silver and alkaline copper solutions and receives a green color from ferric chloride.

Ethyl iodide and caustic alkali convert it (analogous to the deportment of umbelliferon and coumarin) into two isomeric **triethyl-æsculetinic acids** (see above), which are oxidized by MnO_4K into a *triethoxybenzoic acid*, $C_6H_2(O.C_2H_5)_3.CO_2H$, which parts with carbon dioxide and becomes triethoxyhydroquinone, $C_6H_3(O.C_2H_5)_3$ (*Berichte*, 20, 1119).

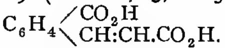
Daphnetin, $C_9H_6O_4$ (see above), is obtained by the decomposition of the glucoside *daphnin*. It is prepared synthetically by the condensation of pyrogallol with malic acid through the action of sulphuric acid (p. 818). It crystallizes in yellow needles or prisms, melting at 255°. It reduces silver and alkaline copper solutions, even in the cold, and receives a green color from ferric chloride. Ethyl iodide and caustic alkali convert it into **triethyl daphnetic acid**, $C_6H_2(O.C_2H_5)_3.C_2H_2.CO_2H$, from which we obtain Triethyl-pyrogallol-carboxylic Acid (p. 782)—*Berichte*, 17, 1089—by means of potassium permanganate.

Unsaturated *dibasic* acids. Under this head may be classed

(1) **Benzal-malonic Acid**, $C_6H_5.CH:C(CO_2H)_2$. This is produced in the condensation of benzaldehyde and malonic acid on digesting with glacial acetic acid (p. 716). It crystallizes from hot water in shining prisms, melting at 196°, with decomposition into carbon dioxide, and cinnamic acid. When it is boiled with water it splits into benzaldehyde and malonic acid; its salts, however, are stable. Sodium amalgam converts it into benzyl-malonic acid (p. 791). Its *diethyl ester*, $C_6H_5.CH:C(CO_2.C_2H_5)_2$, is derived from benzaldehyde and malonic ester by means of HCl or $ZnCl_2$. It boils with slight decomposition about 310° (*Annalen*, 218, 121).

The three *nitrobenzalmalonic acids*, $C_6H_4(NO_2).CH:C(CO_2H)_2$, have been prepared by the condensation of the nitrobenzaldehydes with malonic acid. The ortho-acid yields β-carbostyril carboxylic acid (*Berichte*, 21, Ref. 253) upon reduction with ferrous sulphate.

(2) **Phenyl-maleïc Acid**, $C_6H_5.C_2H(CO_2H)_2$, from phenylmalic acid (p. 792), forms very soluble prisms. It passes into its anhydride at temperatures below 100°. The anhydride melts at 119° (*Berichte*, 23, Ref. 573).

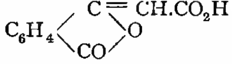

$C_6H_4\left\langle\begin{matrix}CO_2H\\CH:CH.CO_2H\end{matrix}\right.$

(3) **Cinnamyl Carboxylic Acids**, $C_6H_4\left\langle\begin{matrix}CO_2H\\CH:CH.CO_2H.\end{matrix}\right.$ The *ortho*-acid (1, 2), is produced when phthalidacetic acid is digested with alkalies and by carefully oxidizing β-naphthol with potassium permanganate (*Berichte*, 22, Ref. 654). More energetic oxidation produces carbophenyl glyoxylic acid (p. 765). It melts at 174°, and reverts again to phthalidacetic acid.

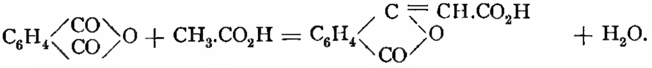
The *para*-acid is obtained from terephthal-aldehydic acid and sodium acetate. It is an insoluble, infusible powder. Nitration converts it into an ortho-nitro acid, which yields indigo-dicarboxylic acid (this is analogous to *o*-nitro-cinnamic acid) (*Berichte*, 19, 948).

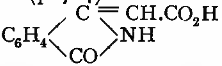
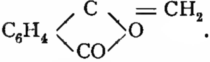
The following are anhydrides (lactones) of *oxydicarboxylic acids*:—

(1) **Phthalyl Acetic Acid**, $C_{10}H_6O_4$ =

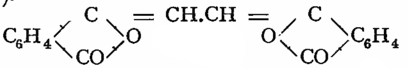
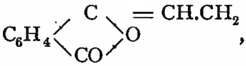

$C_6H_4\left\langle\begin{matrix}C=CH.CO_2H\\ \\CO\end{matrix}\right\rangle O$

, is formed by condensation of phthalic anhydride with sodium acetate (analogous to the reaction of Perkin) (p. 806) (*Berichte*, 17, 2521):—

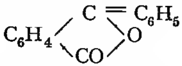

$$C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle O + CH_3.CO_2H = C_6H_4\left\langle\begin{matrix}C=CH.CO_2H\\ \\CO\end{matrix}\right\rangle O + H_2O.$$

It is insoluble in water, soluble with difficulty in alcohol, and melts with decomposition about 243°. Salts of benzoylaceto-carboxylic acid (p. 765) are obtained by dissolving it in alkalies. When it is heated with water to 200° it breaks down into carbon dioxide and aceto-phenone-carboxylic acid (p. 764). When heated with ammonia it forms *Phthalimide Acetic Acid*,  (p. 787); the ethylamines react analogously (*Berichte*, 19, 2368). Phthalyl-acetic acid decomposes by distillation into carbon dioxide and *methylene phthalide*, . This derivative has an odor strongly resembling that of phthalide. It forms vitreous rhombs, melting at 58–60° (*Berichte*, 17, 2522).

Phthalic anhydride forms similar compounds with propionic acid, succinic acid, etc. (*Berichte*, 14, 919).

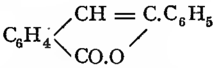
Ethine diphthalyl,  (*Berichte*, 17, 2770), and *Ethidene phthalide*, , very similar to methylene phthalide (*Berichte*, 19, 838), result upon condensation with succinic acid.

Phthalic anhydride and phenylacetic acid, $C_6H_5.CH_2.CO_2H$, condense to *Benzylidene Phthalide* (*Berichte*, 18, 3470), which can be transposed into isomeric *Isobenzal-phthalide* (*Berichte*, 20, 2363):—



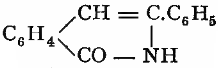
Benzylidene Phthalide.

yields



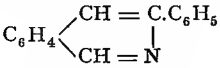
Isobenzalphthalide.

Ammonia converts the latter into *Isobenzal-phthalimidine*, that can be changed to *Phenyl-isoquinoline* (*Berichte*, 18, 3478; 19, 830):

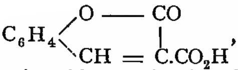


Isobenzal-phthalamidine.

and

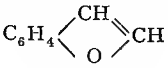


Phenyl-isoquinoline.

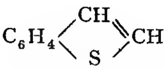
(2) **Coumarin-Carboxylic Acid**, , is produced by condensing salicylic aldehyde and malonic acid upon heating them with glacial acetic acid. It melts at 187°, and about 290° breaks down into carbon dioxide and coumarin (*Berichte*, 19, Ref. 350).

Derivatives of Benzene containing closed Side-chains.

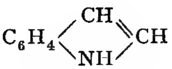
The parent substances of the compounds included in this series are *benzene furfurane* (*coumarone*), *benzothiophene* (*thionaphthene*), and *benzopyrrol* (*indol*):—



Coumarone.



Benzothiophene.



Indol.

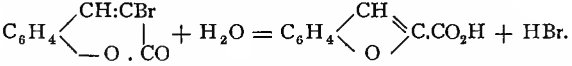
They contain, in addition to the benzene nucleus, a closed chain of five members (as in furfurane, thiophene and pyrrol, p. 521); two of the C-atoms belong to the benzene nucleus.

---

1. BENZOFURFURANE OR COUMARONE GROUP.

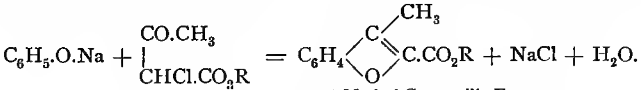
The coumarone compounds are produced:—

(1) By the action of alcoholic potash upon coumarin dibromides or α-brom-coumarins (Fittig, *Annalen*, **126**, 170):—



Other coumarins react similarly. Thus, umbelliferon yields oxycoumarilic acid (*Berichte*, 19, 1783), and æsculetin and daphnetin give dioxycoumarilic acids (*Berichte*, 17, 1075). The coumarones are produced by the elimination of the carboxyl group from the coumarilic acids.

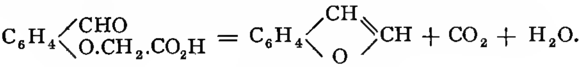
(2) By the action of chloraceto-acetic esters upon the sodium salts of the phenols; β-methyl coumarilic esters result (Hantzsch, *Berichte*, **19**, 1291; 1298):—



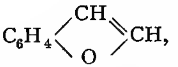
β-Methyl Coumarilic Ester.

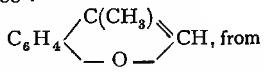
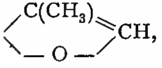
Thus, dimethyl coumarilic acid is derived in this way from para-cresol, and the two naphthols yield two naphthofurfuranes (*Berichte*, 19, 1301). Resorcin and hydroquinone afford benzo-difurfurane, and pyrogallol a benzo-trifurfurane derivative (*Berichte*, 19, 2930; 20, 1332).

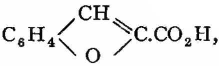
(3) By heating *o*-aldehydo-phenoxy-acetic acid (from salicylaldehyde and chloracetic acid) with sodium acetate (*Berichte*, 17, 3000):—



Coumarone.

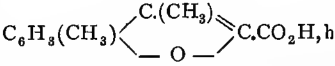
Coumarone, C_8H_6O =  is formed by distilling coumarilic acid with lime. It is present in coal tar (*Berichte*, 23, 78). It is an oil that sinks in water, and boils at 169°. Concentrated acids convert it into a resin. With bromine it yields a dibromide, melting at 88°.

β-Methyl Coumarone, C_9H_8O =  from β-methyl coumarilic acid, is an oil, boiling at 189°. **Dimethyl coumarone**, $C_6H_3(CH_3)$  from dimethyl coumarilic acid, boils at 210°.



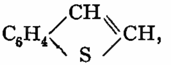
α-**Coumarilic Acid**, $C_9H_6O_3 = C_6H_4\left<\begin{matrix}CH\\O\end{matrix}\right>C.CO_2H$, *α*-coumarone carboxylic acid, is obtained from coumarin dibromide or *α*-brom-coumarin. It crystallizes from hot water in delicate needles, melting at 190° and distils at 310°. It breaks down into salicylic and acetic acids, when fused with caustic potash. It does not combine with bromine or hydrobromic acid. Sodium amalgam converts it into *hydrocoumarilic acid*, $C_9H_8O_3$, melting at 116°, and distilling, with decomposition, at 300°.

β-**Methyl Coumarilic Acid**, $C_9H_5(CH_3)O_3$. Its *ethyl ester* is produced on heating sodium phenoxide with aceto-acetic ester (see above). It melts at 51°, and boils at 290°. The free acid crystallizes from hot water in needles, melting at 189°, and then subliming. If it be rapidly heated it decomposes into carbon dioxide and *β*-methyl coumarone.



Dimethyl Coumarilic Acid, $C_6H_3(CH_3)\left<\begin{matrix}C.(CH_3)\\O\end{matrix}\right>C.CO_2H$, has been prepared from sodium para-cresol with chlor-acet-acetic ester, and from dimethyl coumarin bromide. It melts at 224°, and at higher temperatures decomposes into carbon dioxide and dimethyl coumarone.

2. BENZO-THIOPHENE GROUP.



Benzo-thiophene, $C_6H_4\left<\begin{matrix}CH\\S\end{matrix}\right>CH$, bears the same relation to thiophene as benzofurfurane to furfurane (p. 824). It also bears the same relation to naphthalene that thiophene bears to benzene (the group CH=CH of a benzene nucleus is replaced by a sulphur atom in it), hence it is also known as **Thionaphthene**.

The only known derivative of this series is *α*-**Oxybenzothiophene**, or **Oxythionaphthene**, $C_6H_3(OH)(C_2H_2S)$, corresponding to *α*-naphthol. It is produced by the condensation of thiophenaldehyde and succinic acid (*Berichte*, 19, 1618). It sublimes in long needles, and melts at 72°. It resembles *α*-naphthol in its reactions.

3. BENZOPYRROL OR INDOL GROUP.

This embraces a series of bodies which can be regarded as derivatives of the simplest of them all—of *indol*, C_8H_7N. They were first derived from indigo-blue, and bear an intimate relation to the latter. The most important members are:—

$C_6H_4\left<\begin{matrix}CH\\NH\end{matrix}\right>CH$

Indol.

$C_6H_4\left<\begin{matrix}C(OH)\\NH\end{matrix}\right>CH$

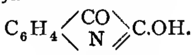
Indoxyl.

$C_6H_4\left<\begin{matrix}CH_2\\NH\end{matrix}\right>CO$

Oxindol.

$C_6H_4\left<\begin{matrix}CH(OH)\\NH\end{matrix}\right>CO$

Dioxindol.



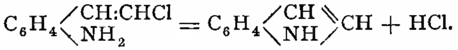
$C_6H_4\left<\begin{matrix}CO\\N\end{matrix}\right>C.OH.$

Isatin.

The last three bodies, so far as concerns their synthetic methods of formation, are amido-anhydrides of ortho-amido-acids of benzene (p. 755). Oxindol is the lactam of *o*-amido-phenyl-acetic acid (p. 755), dioxindol the lactam of *o*-amido-mandelic acid (p. 772), while isatin represents the lactime of *o*-amido-benzoyl-formic acid (p. 762). On the other hand, these three bodies can be converted into each other, and have been obtained from isatin. By complete reduction they may be transformed into indol. All indol-derivatives contain a closed chain, comprising four carbon atoms (two of which belong to the benzene nucleus) and one nitrogen atom (p. 824) analogous to that in pyrrol, hence, indol may be called benzene-pyrrol. In accord with this indol and especially the more stable methyl indols exhibit the reactions of pyrrol (*Berichte*, 19, 2988, 3028). By the rupture of the pyrrol ring (in oxidations, etc.), the indol compounds are changed to ortho-amido-acids of benzene.

Our knowledge of the indol derivatives and their kinship to indigo rests mainly upon the researches of Baeyer (*Berichte*, 13, 2254, 16, 2188).

Indol, C_8H_7N, was first obtained in the distillation of oxindol, and is a product of the reduction of indigo-blue with zinc dust. It is also produced by heating *o*-nitro-cinnamic acid with caustic potash and iron filings. From a theoretical standpoint, the following methods of formation are especially interesting: the reduction of *o*-nitrophenyl-acetaldehyde (p. 721) with zinc dust and ammonia, and the action of sodium alcoholate upon *o*-amido-chlorstyrolene (p. 802):—



$$C_6H_4\left\langle\begin{matrix}CH{:}CHCl\\ NH_2\end{matrix}\right. = C_6H_4\left\langle\begin{matrix}CH\\ NH\end{matrix}\right\rangle CH + HCl.$$

This method represents indol as the anhydride of *o*-amidophenyl-vinyl alcohol, $C_6H_4(NH_2)CH{:}CH(OH)$.

Indol may be obtained by various other methods; thus, by conducting the vapors of the mono- and di-alkyl anilines and ortho-toludines through a tube heated to redness (*Berichte*, 10, 1262); by distilling nitro-propenylbenzoic acid (p. 814) with lime, or phenyl glycocoll with calcium formate; and in the pancreatic fermentation of albuminates, or (together with skatole) in the fusion of the latter with potassium hydroxide, but is best obtained by the first procedure (*Berichte*, 8, 336). A more convenient procedure is to distil α-indol-carboxylic acid (skatole) with lime (*Berichte*, 22, 1976). Another noteworthy formation is that from the quinoline derivatives, *e. g.*, the fusion of carbostyril with potassium hydroxide, or when tetrahydro-quinoline is conducted through a red-hot tube.

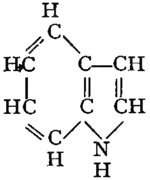
Indol crystallizes from water in shining leaflets, melting at 52° and boiling about 245° with partial decomposition. It is readily volatilized in aqueous vapor. Its vapor density (under diminished pressure) corresponds to the formula C_8H_7N. It possesses a peculiar odor, resembling that of naphthylamine. A pine splinter moistened with hydrochloric acid and dipped into its alcoholic solution acquires a cherry-red color. Indol possesses but very feeble basic properties (similar to pyrrol), and is scarcely dissolved by dilute hydrochloric acid. Hot acids resinify it very readily.

On adding sodium nitrite to a solution of indol in acetic acid (90%) the latter assumes a deep red color owing to the formation of *Nitroso-indol*, $C_8H_6N(NO)$ yellow crystals, melting at 172° (*Berichte*, 23, 2299).

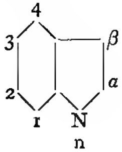
β-Aceto-indol, *nβ-Diaceto-indol* (*Berichte*, 22, 1977), and *n-Aceto-indol* (*Berichte*, 23, 1359, 2296) are all produced upon heating indol (and *a*-indol-carboxylic acid) to 180° with acetic anhydride.

Alkyl Indols.

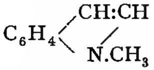
These are derived by replacing the hydrogen of indol by alkyls. Their isomerides can be readily deduced from the following scheme :—



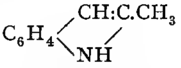
or



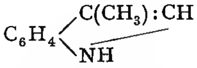
It corresponds to that given to pyrrol. The benzene hydrogen atoms are marked by the numbers 1 to 4. The substitution products derived from the pyrrol nucleus can exist in three isomeric forms; they are designated, as with the pyrrol derivatives, *n*-, *a*- and *β* :—



n-Methyl Indol.



a-Methyl Indol.



β-Methyl Indol.

E. Fischer terms the derivatives of the pyrrol nucleus *Py*-(1, 2, 3)-derivatives, those of the benzene nucleus B-(1, 2, 3, 4)-derivatives (*Annalen*, 236, 121; *Berichte*, 19, Ref. 829).

The alkyl indols may be synthesized :—

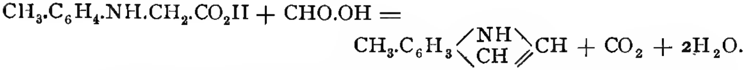
(1) By the production of closed rings from *o*-amido-compounds (p. 827): *o*-amidobenzylmethyl ketone forms *a*-methyl indol (p. 729); *o*-amidochlorstyrolene, $C_6H_4\langle\begin{smallmatrix}CH:CHCl\\NH.CH_3\end{smallmatrix}$, yields *n*-methyl indol; while *a*-phenyl indol is obtained from *o*-nitrodesoxybenzoin, $C_6H_4\langle\begin{smallmatrix}CH_2.CO.C_6H_5\\NO_2\end{smallmatrix}$.

(2) By heating the anilines with compounds, containing the group—CO.CHCl. For example, aniline and chloraldehyde form indol; with chloracetone, $CH_3.CO.CH_2Cl$, the product is *a*-methyl indol, and with *β*-bromlævulinic acid, $CH_3.CO.CHBr.CH_2.CO_2H$, *aβ*-dimethyl indol is the product. The alkyl anilines and toluidines (*Berichte*, 21, 3360) react in a similar manner.

The reaction does not always pursue the same course; thus, aniline and bromacetophenone, heated together, yield *a*-phenyl indol and not the *β*-product. This is very probably due to the fact that the first product is $C_6H_5.C(N.C_6H_5).CH_2Br$

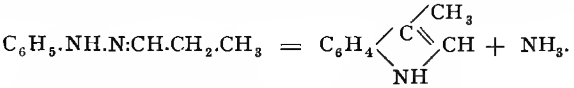
(*Berichte*, 21, 1076). Similarly, *n*-methyl-*a*-phenyl indol is formed from brom-acetophenone (*Berichte*, 21, 2595).

(3) Upon heating together phenylglycocolls and calcium formate. In this way, phenylglycocoll, $C_6H_5.NH.CH_2.CO_2H$, yields indol and tolyl glycocoll, toluindol (*Berichte*, 23, Ref. 654):—



$$CH_3.C_6H_4.NH.CH_2.CO_2H + CHO.OH = CH_3.C_6H_3\left\langle\begin{matrix}NH\\CH\end{matrix}\right\rangle CH + CO_2 + 2H_2O.$$

4. A noteworthy and excellent method for the production of the alkyl indols consists in condensing the phenylhydrazones of the aldehydes, ketones and ketonic acids (p. 656) by heating them with hydrochloric acid or zinc chloride (E. Fischer, *Berichte*, 19, 1563; 22, Ref. 14). The compounds of β-methyl-phenylhydrazine behave similarly (p. 657). Thus, propylidene phenylhydrazone yields β-methyl indol:—

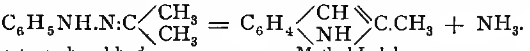


$$C_6H_5.NH.N{:}CH.CH_2.CH_3 = C_6H_4\left\langle\begin{matrix}C(CH_3)\\NH\end{matrix}\right\rangle CH + NH_3.$$

Propylidene-phenyl-hydrazone. β-Methyl Indol.

Phenylacetaldehyde, $C_6H_5.CH_2.CHO$, in like manner yields β-phenyl indol.

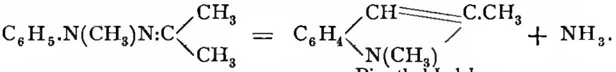
a-Methyl indol is prepared from acetone-phenylhydrazone:—



$$C_6H_5NH.N{:}C\left\langle\begin{matrix}CH_3\\CH_3\end{matrix}\right. = C_6H_4\left\langle\begin{matrix}CH\\NH\end{matrix}\right\rangle C.CH_3 + NH_3.$$

Acetone-phenyl-hydrazone. a-Methyl Indol.

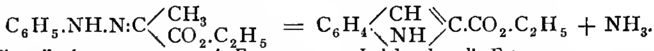
na-Dimethyl indol is derived from acetone-methyl-phenyl-hydrazone:—



$$C_6H_5.N(CH_3)N{:}C\left\langle\begin{matrix}CH_3\\CH_3\end{matrix}\right. = C_6H_4\left\langle\begin{matrix}CH=C.CH_3\\N(CH_3)\end{matrix}\right. + NH_3.$$

na–Dimethyl Indol.

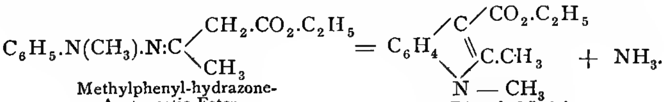
The first products from phenylhydrazine and the a- and γ-ketonic acids (better their esters) are the *indol carboxylic acids* (and their esters); these lose carbon dioxide and pass into indols:—



$$C_6H_5.NH.N{:}C\left\langle\begin{matrix}CH_3\\CO_2.C_2H_5\end{matrix}\right. = C_6H_4\left\langle\begin{matrix}CH\\NH\end{matrix}\right\rangle C.CO_2.C_2H_5 + NH_3.$$

Phenylhydrazone-pyroracemic Ester. a-Indol-carboxylic Ester.

The β-alkylhydrazine derivatives react very easily with pyroracemic acid, upon warming them with dilute hydrochloric acid, sulphuric or phosphoric acid; the products are *n* alkyl-indol-carboxylic acids. When the phenylhydrazine derivatives of the β-ketonic acids, *e. g.*, aceto-acetic ester, are heated with zinc chloride they are principally converted into pyrazole compounds (p. 656). On the other hand, compounds of acetoacetic ester and β-alkylhydrazines (which cannot form pyrazole compounds) yield indol derivatives with zinc chloride:—



$$C_6H_5.N(CH_3).N{:}C\left\langle\begin{matrix}CH_2.CO_2.C_2H_5\\CH_3\end{matrix}\right. = C_6H_4\left\langle\begin{matrix}C(CO_2.C_2H_5)\\N-CH_3\end{matrix}\right\rangle C.CH_3 + NH_3.$$

Methylphenyl-hydrazone-
Acetoacetic Ester.

na-Dimethyl Indol
Carboxylic Ester.

See *Annalen*, 239, 223 for the indols from tolyl and naphthyl hydrazones.

Nearly all the alkyl indols possess the fæcal odor of indol. The odor of the *n*-methyl indols is similar to that of methyl aniline. The phenyl indols and indol carboxylic acids are non-volatile and odorless. They are more stable toward acids than indol, dissolve in concentrated hydrochloric acid, and are reprecipitated unaltered by water. Picric acid unites with all of them, forming compounds, crystallizing in red needles (distinction from the pyrrols, *Berichte*, 21, 3299). Most of the indol derivatives give the pine-shaving reaction, the exceptions being the indol carboxylic acids and the *αβ*-dialkyl indols (*Berichte*, 21, 3300). It is only the *β*-alkyl- and *αβ*-dialkylindols that yield simple nitroso-compounds with nitrous acid (*Berichte*, 23, 2299).

The methyl indols, like pyrrol, combine with aldehydes, acid anhydrides and diazo-compounds (*Berichte*, 20, Ref. 429; 21, Ref. 18). *Red* dye-stuffs, resembling fuchsine and called rosindols (*Berichte*, 20, 815), are produced by heating *n*-, *α*- and *β*-methyl indol with benzene chloride and zinc chloride.

Interesting transformations are those of methyl indols and indol into quinoline derivatives (similar to formation of pyridine compounds from pyrrol, p. 541). In this change a methylene group pushes itself into the pyrrol ring, and the resulting pyridine ring is then further methylated. The conversion ensues upon heating the compounds with chloroform and sodium alcoholate (*Berichte*, 21, 1940), or with alkyl iodides (*Berichte*, 20, 2199). In this manner *α*- and *β*-methyl indol as well as indol together with methyl iodide at 130° yield trimethyl-dihydroquinoline:—

$$C_8H_8N(CH_3) + 3CH_3I = C_9H_8N(CH_3)_3 + 3HI$$ (*Berichte*, 23, 2629; 22, 1979).

n-Acetyl- and *β*-acetyl-*α*-methyl indol are produced upon boiling *α*-methyl indol with acetic anhydride, while *α*-acetyl-*β*-methyl indol is obtained by like treatment from *β*-methyl indol. Boiling hydrochloric acid causes the elimination of the acetyl groups (*Berichte*, 21, 1936).

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n-**Methyl Indol**, $C_8H_6N(CH_3)$, may be obtained by heating *n*-methyl-indol carboxylic acid to 200°. It is an oil, boiling at 239°. *n*-**Ethyl Indol**, $C_8H_6N.C_2H_5$ (boiling at 247°), is prepared the same as the preceding compound. Sodium hypobromite oxidizes both compounds, forming methyl and ethyl pseudo-isatin. *n*-**Phenyl Indol**, $C_8H_6N(C_6H_5)$, from *n*-phenyl-indol-carboxylic acid, is a heavy oil. It imparts an intense, bluish-violet color to a pine shaving (*Berichte*, 17, 568).

α-**Methyl Indol**, $C_8H_5(CH_3)NH$, **Methyl Ketol**, arises in the anhydride-formation of *o*-amido-benzyl-methyl ketone (p. 729), and is very easily prepared by heating acetone phenylhydrazone with zinc chloride to 180° (see above). It crystallizes from ligroïne in colorless needles or leaflets, melting at 59°. Its odor is like that of indol, and its reactions are similar. Oxidation with MnO_4K (by rupture of the pyrrol ring at the point of the double binding) converts it into aceto-*o*-amido-benzoic acid (p. 749). *α*-Indol carboxylic acid is formed when it is fused with caustic potash.

α-**Phenyl Indol**, $C_8H_5(C_6H_5)NH$, may be formed from acetophenone phenylhydrazone (p. 728) by fusion with zinc chloride, from *o*-nitro-desoxybenzoin (p. 828) by reduction, by the action of aniline upon brom-acetophenone, and from phenylacetaldehyde-phenylhydrazone by the molecular rearrangement of the *β*-phenyl-indol, which first forms. It crystallizes from alcohol in colorless leaflets and melts at 187°

β-**Methyl Indol**, $C_8H_5(CH_3)NH$, *Skatole*, occurs in human fæces (with a little indol). It may be obtained, together with indol, from reduced indigo (p. 827), by the putrefaction of albuminoids, or (with indol) in the fusion of the same with potassium hydroxide. See *Berichte*, 18, Ref. 80, for the isolation of indol. In the putrefaction skatole carboxylic acid, $C_9H_8N.CO_2H$, first results; this melts at 161°, and decomposes into carbon dioxide and skatole. It was first synthesized by distilling nitrocumic acid with zinc dust. It can be prepared without difficulty by heating propidene-phenylhydrazone with zinc chloride (p. 829). It crystallizes from ligroïne in leaflets, melting at 95°, and boils at 265°. It has a penetrating fecal odor. For the reaction with a pine shaving, see *Annalen*, 236, 140.

β-**Phenyl Indol**, $C_8H_5(C_6H_5)NH$, may be prepared by heating phenyl-acetaldehyde-phenylhydrazone, $C_6H_5.CH_2.CH:N_2H.C_6H_5$, with alcoholic hydrochloric acid (isomeric α-phenylindol is formed by fusion with zinc chloride). It forms white leaflets, melting at 89° (*Berichte*, 21, 1811). Various methyl-phenyl indols sustain analogous transpositions (*Berichte*, 22, Ref. 672).

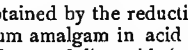
Indol Carboxylic Acids.

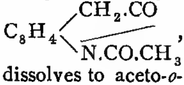
These are produced (p. 829) when indol and alkyl indols are heated with sodium and carbon dioxide (similar to the pyrrol carboxylic acids, *Berichte*, 21, 1925); further by fusing the alkyl indols with caustic alkali. Ordinary oxidizing agents do not attack them (*Berichte*, 21, 1929, 1937). Heated alone or with lime they break down into carbon dioxide and indols.

α-**Indol Carboxylic Acid**, $C_8H_5N.CO_2H$, from pyroracemic-phenyl hydrazone and from α-methyl indol, crystallizes from hot water in delicate needles, melting at 200°, and decomposing into carbon dioxide and indol.. It yields *imide* anhydride, $C_{18}H_{10}N_2O_2$ (*Berichte*, 22, 2503) if heated with acetic anhydride. *n-Methyl-* and *n-Ethyl-α-indol-carboxylic acid*, $C_8H_5N(CH_3)CO_2H$, are produced from pyrosuccinnic acid with methyl and ethyl hydrazine (p. 829). They break down when fused into carbon dioxide and methyl- and ethyl-indol.

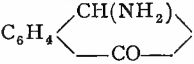
β-**Methyl-α-Indol Carboxylic Acid**, $C_8H_5(CH_3)N.CO_2H$, skatole carboxylic acid, results from the decay of albuminates. It crystallizes in leaflets, melting at 165°, and decomposing into carbon dioxide and skatole. Another product, formed at the time, is *Skatole Acetic Acid*, $C_8H_5(CH_3)N.CH_2.CO_2H$, melting at 130° (*Berichte*, 22, Ref. 701).

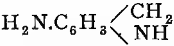
β-**Indol Carboxylic Acid**, $C_9H_8N.CO_2H$, is produced when skatole is fused with caustic potash, and upon heating indol with sodium in a current of carbon dioxide at 230–300° (together with a little of the α-acid). It crystallizes from hot water in leaflets and melts with decomposition at 218°. Being a β-acid it cannot yield an imide anhydride (*Berichte*, 23, 2296). *na*-Dimethyl-β-indol carboxylic acid, $C_8H_4(CH_3)N(CH_3).CO_2H$, from methyl-phenylhydrazone-acetoacetic ester (p. 829), melts at 200°, and decomposes into carbon dioxide and *na*-dimethyl indol.

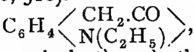
Oxindol, C_8H_7NO =  $C_6H_4\langle{}^{CH_2}_{NH}\rangle CO$, the lactam of *o*-amido-phenyl acetic acid (p. 755), was first obtained by the reduction of dioxindol with tin and hydrochloric acid, or with sodium amalgam in acid solution. It is also produced in the reduction of aceto-*o*-amido-mandelic acid (p. 774) with hydrochloric acid. It crystallizes from hot water in colorless needles, and melts at 120°. It oxidizes to dioxindol when exposed in a moist condition; by protracted boiling it will reduce an ammoniacal silver solution. It has both basic and weak acid properties, forms a stable hydrochloride, and dissolves in alkalies. If heated to 150° with baryta water it is converted into *o*-amido-phenyl-acetic acid (p. 756).

Oxindol boiled with acetic anhydride yields *Aceto-oxindol*,  $C_8H_4\langle{}^{CH_2.CO}_{N.CO.CH_3}\rangle$, which crystallizes in long needles, and melts at 126°. It dissolves to aceto-*o*-

amido-phenyl acetic acid in sodium hydroxide (p. 756). The action of nitrous acid upon the aqueous solution of oxindol causes a transposition and isatoxime results (p. 837); this was formerly taken for *nitroso-oxindol;* the latter passes, by reduction with tin and hydrochloric acid, into the so-called **Amido-oxindol**,


$C_6H_4\left\langle\begin{matrix}CH(NH_2)\\ CO\end{matrix}\right\rangle CO$ (?). Ferric chloride oxidizes this to isatin.

An isomeride of the last compound is  $H_2N.C_6H_3\left\langle\begin{matrix}CH_2\\ NH\end{matrix}\right\rangle CO$, *p*-**Amido-oxindol**, which is produced by the reduction of dinitrophenyl-acetic acid (p. 754). Isatoxime also results from it when it is acted upon by nitrous acid and boiled with alcohol (*Berichte*, 16, 518).

Ethyl Oxindol  $C_6H_4\left\langle\begin{matrix}CH_2.CO\\ N(C_2H_5)\end{matrix}\right\rangle$, is obtained on boiling oxindol with sodium ethylate (1 equivalent) and ethyl iodide. It is an oil, volatile with aqueous vapor. If it be heated with baryta water or with concentrated hydrochloric acid to 150° the ethyl group will not be split off (compare p. 755) (*Berichte*, 16, 1705).

Indoxyl and pseudo-indoxyl are isomeric with oxindol. The second is only stable in its derivatives; the two forms are therefore probably tautomeric:—


$C_6H_4\left\langle\begin{matrix}C(OH)\\ NH\end{matrix}\right\rangle CH$

Indoxyl.

and


$C_6H_4\left\langle\begin{matrix}CO\\ NH\end{matrix}\right\rangle CH_2$.

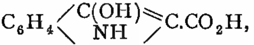
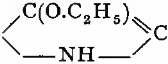
Pseudoindoxyl.

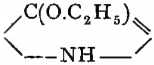
Indoxyl, C_8H_7NO, results in the elimination of carbon dioxide from indoxylic acid (see below). This is best effected by boiling with water. It is an oil not volatile in aqueous vapor, and is rather easily soluble in water, showing yellow fluorescence. It is very unstable, and in aqueous or slightly acid solution is readily resinified. It dissolves with a red color in concentrated hydrochloric acid. It is oxidized to *indigo blue* when its alkaline solution (best ammoniacal) is exposed to the air. Ferric chloride and hydrochloric acid effect the conversion more quickly:—

$$2C_8H_7NO + 2O = C_{16}H_{10}N_2O_2 + 2H_2O.$$

When indoxyl is digested with potassium pyrosulphate, $S_2O_7K_2$ (compare p. 670), we get potassium indoxylsulphate, $C_8H_6N.O.SO_3K$, which crystallizes from hot alcohol in shining leaflets. This is found in the urine of herbivorous animals (Urine indican), generally after the ingestion of indol. When digested with acids the salt decomposes into sulphuric acid and indoxyl, which forms indigo blue by the addition of a little ferric chloride (an excess of ferric chloride destroys the indigo). We proceed similarly in the detection of indoxylsulphuric acid in urine.

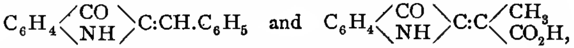
The presence of the imide group in indoxyl is proven by the formation of a *nitrosamine* and a phenyl-diazo compound (*Berichte*, 16, 2190); the existence of a phenol-like hydroxyl is inferred from the production of indoxylsulphuric acid and of ethyl-indoxyl (see below).

Indoxylic Acid, $C_9H_7NO_3$ =  $C_6H_4\left\langle\begin{matrix}C(OH)\\ NH\end{matrix}\right\rangle C.CO_2H$, corresponding to indoxyl, is produced from its ethyl ester by fusion with caustic soda at 180° (*Berichte*, 17, 976). Acids precipitate it from its salts in the form of a white crystalline precipitate. It melts at 123°, with decomposition into carbon dioxide and indoxyl. Like the latter, it is oxidized to indigo blue. Its *ethyl ester* is obtained by reducing *o*-nitrophenyl propiolic ester with ammonium sulphide, or isatogenic ester with zinc and hydrochloric acid and from indoxanthic ester (p. 833). It crystallizes in thick prisms, and melts at 120°. When digested with sulphuric acid it affords a quantitative yield of *indigo-sulphonic acid*. It possesses a phenol character, dissolves in alkalies and is again precipitated by carbon dioxide. Ethyl iodide converts the phenol salts into **Ethyl Ethoxy-indoxylic Ester**,  $C_6H_4\left\langle\begin{matrix}C(O.C_2H_5)\\NH\end{matrix}\right\rangle C.CO_2.C_2H_6$, which by saponification with baryta water, forms **Ethoxy-indoxylic Acid.** The latter consists of brilliant needles, melting at 160°. It yields indoxyl when digested with hydrochloric acid (just as in the case of ethyl indoxyl), and this gives indigo blue with ferric chloride.

If fused it separates into carbon dioxide and ethoxy-indoxyl,  $C_6H_4\left\langle\begin{matrix}C(O.C_2H_5)\\NH\end{matrix}\right\rangle CH$. The latter is an oil, volatile in steam, and having an odor like that of indol, which it resembles in other respects. Nitrous acid converts it into a nitrosamine (*Berichte*, 15, 781).

Pseudo-indoxyl (see above) is known only in its derivatives. Its *isonitroso*-compound, $C_6H_4\left\langle\begin{matrix}CO\\NH\end{matrix}\right\rangle C(N.OH)$, formerly considered *nitroso-indoxyl*, is produced by the action of nitrous acid upon ethoxyindoxylic acid. A transposition occurs here. It is identical with pseudo-isatoxime (p. 837).

The derivatives of pseudo-indoxyl—

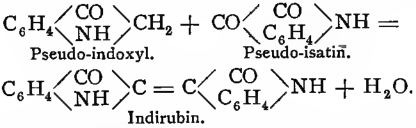


$$C_6H_4\left\langle\begin{matrix}CO\\NH\end{matrix}\right\rangle C{:}CH.C_6H_5 \quad \text{and} \quad C_6H_4\left\langle\begin{matrix}CO\\NH\end{matrix}\right\rangle C{:}C\left\langle\begin{matrix}CH_3\\CO_2H\end{matrix}\right.,$$

are similarly obtained from indoxyl or indoxylic acid by condensation with benzaldehyde and pyroracemic acid. They are called the *indogenides* of the latter compound, and are perfectly similar to *pseudo-isatin ethoxime* (p. 837). The divalent group, $C_6H_4\left\langle\begin{matrix}CO\\NH\end{matrix}\right\rangle C=$, is termed *indogen* (*Berichte*, 16, 2197).

The condensation of isatin with benzenes produces perfectly analogous indogenides. In this case the isatin changes to pseudo-isatin, $C_6H_4\left\langle\begin{matrix}CO\\NH\end{matrix}\right\rangle CO$.

Indirubin, $C_{16}H_{10}N_2O_2$, is of this class. It is isomeric with indigo-blue, and appears in nearly all the indigo syntheses, and in its entire character is very similar to this substance. It is produced by effecting the condensation of indoxyl (pseudo-indoxyl) with isatin (pseudo-isatin) by means of a dilute soda solution (*Berichte*, 17, 976), and therefore, may be called an indogenide of pseudo-isatin:—



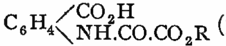
$$C_6H_4\left\langle\begin{matrix}CO\\NH\end{matrix}\right\rangle CH_2 + CO\left\langle\begin{matrix}CO\\C_6H_4\end{matrix}\right\rangle NH =$$

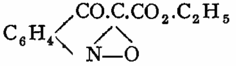
Pseudo-indoxyl. Pseudo-isatin.

$$C_6H_4\left\langle\begin{matrix}CO\\NH\end{matrix}\right\rangle C = C\left\langle\begin{matrix}CO\\C_6H_4\end{matrix}\right\rangle NH + H_2O.$$

Indirubin.

In the same manner indoxyl may be oxidized (by the union of two pseudo-indoxyl groups with separation of water) to indigo-blue, which, therefore, is to be considered a *di-indogen* (*Berichte*, 16, 2204).

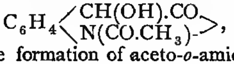
Indoxanthic Ester, $C_{11}H_{11}NO_4 = C_6H_4\left\langle\begin{matrix}CO\\NH\end{matrix}\right\rangle C(OH).CO_2.C_2H_5$, results from the oxidation of indoxylic ester with ferric chloride or chromic acid. It yields a nitrosamine with nitrous acid (*Berichte*, 15, 774). Further oxidation produces anthranil oxalylic ester,  $C_6H_4\left\langle\begin{matrix}CO_2H\\ NH.CO.CO_2R\end{matrix}\right.$ (p. 749)—this is analogous to the formation of aceto-anthranilic acid (p. 830) from methyl ketol. Indoxanthic ester reverts to indoxylic ester when reduced.

Isatogenic Ester, $C_{11}H_9NO_4$ =  $C_6H_4\left\langle\begin{matrix}CO.C.CO_2.C_2H_5\\ \diagup\diagdown\\ N—O\end{matrix}\right.$ (?), is obtained by a transposition of the isomeric *o*-nitrophenyl propiolic ester when it dissolves in concentrated sulphuric acid (p. 815). It crystallizes in yellow needles, melting at 115°. Various reducing agents convert it into indoxylic ester, but with ferrous sulphate we get indoxanthic ester. In the solution of free *o*-nitrophenyl acetic acid in sulphuric acid, the free **Isatogenic Acid**, $C_8H_4.NO_2.CO_2H$, is very probably produced; it cannot, however, be isolated. Isatin, $C_8H_5NO_2$, exists in the solution diluted with water.

Di-isatogen, $C_{16}H_8N_2O_4$, isomeric with the preceding, is similarly formed by dissolving *o*-dinitrophenyl-diacetylene (p. 802) in sulphuric acid (by the union of two isatogen groups, $C_6H_4:(C_2NO_2)$. It crystallizes in red needles and by reduction yields *indigo-blue*:—

$$C_{16}H_8N_2O_4 + 3H_2 = C_{16}H_{10}N_2O_2 + 2H_2O.$$

On adding sulphate of iron to the solution of isatogenic ester, di-isatogen or *o*-nitrophenyl propiolic acid in sulphuric acid, the solution becomes blue in color and **Indoïn**, $C_{32}H_{20}N_4O_5$ (?), separates. This is very similar to indigo-blue. It is also formed by adding *o*-nitrophenyl propiolic acid to the solution of indoxyl or indoxylic acid in sulphuric acid.

Di-oxindol, $C_8H_7NO_2$ =  $C_6H_4\left\langle\begin{matrix}CH(OH)\\ NH\end{matrix}\right\rangle CO$, is the lactam of *o*-amido-mandelic acid, not capable of existing in a free condition, or hydrindic acid (p. 773). It is more readily obtained by boiling isatin with zinc dust, water and a slight quantity of hydrochloric acid. It is rather easily soluble in water and alcohol, crystallizes in colorless prisms, melting at 180° and decomposing about 195° with formation of aniline. It oxidizes readily in aqueous solution to *isatid* and *isatin*. It forms salts with bases and acids; it combines with two equivalents of the former. Nitrous acid converts it into the nitroso-compound, $C_8H_6(NO)NO_2$, melting at 300° and subliming in white needles. Di-oxindol heated with acetic anhydride to 140° yields *aceto-oxindol*  $C_6H_4\left\langle\begin{matrix}CH(OH).CO\\ N(CO.CH_3)\end{matrix}\right\rangle$, melting at 127°, and dissolving in baryta water with the formation of aceto-*o*-amido-mandelic acid (p. 774).

Isatin, $C_8H_5NO_2$, is the lactime of *o*-amido-phenyl-glyoxylic acid or *isatinic acid* (p. 762), whose lactam, the hypothetical *pseudo-isatin*, is known only in its derivatives:—

$C_6H_4\left\langle\begin{matrix}CO\\ N\end{matrix}\right\rangle C.OH$

Isatin.

$C_6H_4\left\langle\begin{matrix}CO.CO\\ NH\end{matrix}\right\rangle$.

Pseudo-isatin.

Isatin was first obtained by the oxidation of indigo. It is also prepared from oxindol by transposition into the so-called amido-oxindol (p. 831) and then oxidizing the latter with ferric chloride. It arises in a similar manner from indoxyl. Its ready formation from *o*-nitro-phenyl-propiolic acid by boiling with alkalies (p. 815), and by the decomposition of isatogenic acid (p. 834), is worthy of remark. It is also obtained from α-oxyquinoline (carbostyril) in its oxidation with potassium permanganate.

The easiest method of preparing isatin consists in oxidizing indigo with nitric acid (*Berichte*, 17, 976). To purify it, dissolve it in potassium hydroxide, add hydrochloric acid as long as a black precipitate is formed, and then treat the filtrate with hydrochloric acid.

Isatin crystallizes in yellowish-red monoclinic prisms, melting at 201°, and subliming partially undecomposed. It dissolves in water and alcohol with a reddish-brown color. It dissolves in caustic alkalies (equivalent quantities), forming salts, *e. g.*, $C_8H_4NKO_2$. The solution, violet at first, soon becomes yellow, with the production of isatinates; digestion with excess of alkali causes the immediate transformation. Acids liberate the readily soluble isatinic acid from its salts; and on standing, more quickly upon the application of heat, this changes to isatin, at the same time assuming a yellowish-red color. Isatin also possesses a ketone-like character; it unites with alkaline bisulphites to crystalline compounds, with hydroxylamine to isatoxime (p. 837), and with phenyl-hydrazine hydrochloride to a yellow compound, melting at 210°, which may be employed in detecting isatin (*Berichte*, 17, 577).

Isatin unites with phenylisocyanate, forming carbanilido-isatin. It affords a dark blue solution with benzene containing thiophene and sulphuric acid (p. 530). Water precipitates a blue dye, *indophenin*, $C_{12}H_7NOS = (C_8H_5NO_2 + C_4H_4S - H_2O)$ (*Berichte*, 18, 2638).

Two molecules of phenol, toluene or dimethyl-aniline and isatin are condensed by concentrated sulphuric acid to colorless compounds, derivatives of pseudo-isatin,

$$C_6H_4\left\langle\begin{matrix} C(R)_2.CO \\ NH \end{matrix}\right\rangle$$

(*Berichte*, 18, 2639).

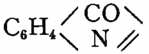
Isatoic acid is formed when isatin is oxidized with chromic acid in glacial acetic acid solution (p. 749).

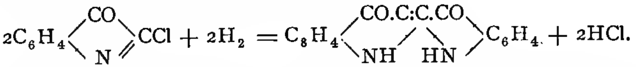
Isatin yields nitrosalicylic acid when oxidized with nitric acid, and aniline when fused with potassium hydroxide. When reduced (boiling with zinc dust, etc.), it first becomes dioxindol (a derivative of pseudo-isatin); with ammonium sulphide we get an intermediate product—isatid, $C_{16}H_{12}N_2O_4$. This is a colorless powder, readily re-oxidizing to isatin.

In a solution of potassium-isatin, or in one of ammonia containing isatin, silver nitrate precipitates *silver isatin*, $C_8H_4AgNO_2$, a red compound. Chlorine and bromine (in glacial acetic acid) convert isatin into substitution products, which conduct themselves just like isatin, and if dissolved in alkalies yield substituted isatinic acids. Nitration in the cold produces *nitroisatin*, $C_8H_4(NO_2)NO_2$—red needles, melting at 230°.

If ammonia should act upon isatin suspended in ether, there will result **Imesatin**, $C_8H_5NO(NH)$, forming dark yellow crystals, and when digested with alkalies or acids, decomposing again into isatin and NH_3. **Tolyl-methylimesatin**,

$C_8H_4(CH_3)NO(N.C_7H_7)$, is an analogous compound. It contains the residue of para toluidine, $C_6H_4(CH_3)N =$, in place of the NH-group. It is obtained by heating *p*-toluidine with dichloracetic acid (by condensation) (*Berichte*, **16**, 2261). Concentrated hydrochloric acid decomposes it (like imesatin) into toluidine and *p*-**Methylisatin**, $C_8H_4(CH_3)NO_2 = C_6H_3(CH_3).C_2NO_2H$. The latter resembles isatin; with PCl_5 it affords *p*-**Methylisatin chloride**, $C_8H_4(CH_3)NOCl$, which (in the same manner as isatin chloride, etc.), may be converted into **dimethyl indigo-blue**, $C_{16}H_8(CH_3)_2N_2O_2$ (methylated in the benzene nucleus).

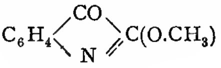
Isatin Chloride,  $C_6H_4\left\langle\begin{array}{c}CO\\N\end{array}\right\rangle CCl$, is produced by digesting isatin with PCl_5 (in benzene solution). It crystallizes in brown needles and dissolves with a blue color in ether, alcohol and glacial acetic acid. Hydriodic acid or zinc dust acting on its glacial acetic acid solution produces *indigo-blue*:—



$$2C_6H_4\left\langle\begin{array}{c}CO\\N\end{array}\right\rangle CCl + 2H_2 = C_8H_4\left\langle\begin{array}{c}CO.C:C.CO\\NH \quad HN\end{array}\right\rangle C_6H_4 + 2HCl.$$

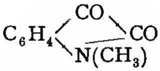
We can also obtain from the substituted isatins (brom-, nitro-, methyl-isatin) substitution products of indigo blue, dibrom-, dinitro, and dimethyl-indigo-blue (*Berichte*, **12**, 456).

Ether derivatives of isatin and pseudo-isatin:—



$$C_6H_4\left\langle\begin{array}{c}CO\\N\end{array}\right\rangle C(O.CH_3)$$

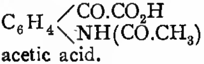
Methyl-isatin.

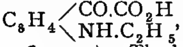


$$C_6H_4\left\langle\begin{array}{c}CO\\N(CH_3)\end{array}\right\rangle CO$$

Methyl-pseudo-isatin.

The *alkyl isatins* result from the action of alkyl iodides upon silver-isatin, and are blood-red colored crystalline bodies. **Methyl-isatin**, $C_6H_4NO_2(CH_3)$, melts at 102°. **Ethyl dibrom-isatin**, $C_8H_2Br_2NO_2(C_2H_5)$, at 88°. They are saponified by alkalies, and yield salts of isatin and isatinic acid. Acids separate isatin from these. Ammonium sulphide with air contact converts them at once into indigo blue (*Berichte*, **15**, 2093).

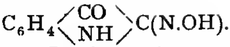
When isatin is boiled with acetic anhydride a transposition occurs and we obtain **Aceto-pseudo-isatin**,  $C_6H_4\left\langle\begin{array}{c}CO.CO\\N(CO.CH_3)\end{array}\right\rangle$, crystallizing in yellow needles, and melting at 141°. When digested with water or acids it splits into acetic acid and isatin. It dissolves in alkalies, forming salts of aceto-isatinic acid,  $C_6H_4\left\langle\begin{array}{l}CO.CO_2H\\NH(CO.CH_3)\end{array}\right.$ (p. 762), which decompose on warming into isatinates and acetic acid.

Ethylpseudoisatin (see above) is obtained by the reduction and subsequent oxidation of ethoxypseudo-isatin-ethoxime (see below). It crystallizes in large, blood-red crystals, melting at 95°. It dissolves immediately in alkalies with a yellow color, forming salts of ethyl isatinic acid,  $C_8H_4\left\langle\begin{array}{l}CO.CO_2H\\NH.C_2H_5\end{array}\right.$, from which acids at once separate ethylpseudo-isatin (*Berichte*, **16**, 2193). The latter is also obtained from ethyl indol (p. 830), by oxidation with a hypobromite (*Berichte*, **17**, 566). **Methyl-pseudoisatin**, formed in the same way, consists of red needles, melting at 134°.

Isonitroso-derivatives of Isatin and Pseudoisatin:—


$C_6H_4\left\langle\begin{array}{l}C(N.OH)\\N\end{array}\right\rangle C.OH$

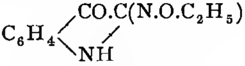
Isatoxime.


$C_6H_4\left\langle\begin{array}{l}CO\\NH\end{array}\right\rangle C(N.OH).$

Pseudo-isatoxime.

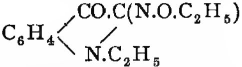
Isatoxime, $C_8H_6N_2O_2$ (Isatin-oxime), was first obtained by the action of nitrous acid upon oxindol (p. 831), and was, therefore, formerly considered nitroso-oxindol. It is also prepared (analogous to the formation of the acetoximes, from isatin and hydroxylamine; or from para-amido-oxindol (p. 832), by action of nitrous acid, and boiling with alcohol (*Berichte*, 16, 518). It crystallizes from alcohol in yellow needles, and melts at 202°, with decomposition. It dissolves with a yellow color in the alkalies. When reduced with tin and hydrochloric acid it yields so-called amido-oxindol (p. 832). By the successive action of ethyl iodide upon the silver salt we obtain a mono-, and a diethyl derivative from which isatin (*Berichte*, 16, 1706) is formed by reduction and subsequent oxidation.

Pseudo-isatoxime (see above) is prepared (by transposition) by the action of nitrous acid upon ethyl indoxylic acid. It was formerly considered nitroso-indoxyl (p. 833). It crystallizes from alcohol in shining yellow needles, and decomposes at about 200°. It does not give the nitroso reaction. It dissolves in alkalies and is separated again by carbon dioxide (*Berichte*, 15, 782). Ethyl iodide and sodium ethylate convert it into:—

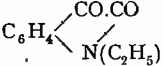

$C_6H_4\left\langle\begin{array}{l}CO.C(N.O.C_2H_5)\\NH\end{array}\right.$

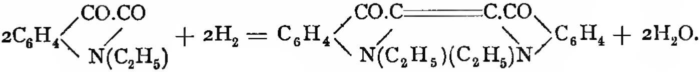
Pseudoisatin-ethoxime.

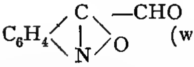
and


$C_6H_4\left\langle\begin{array}{l}CO.C(N.O.C_2H_5)\\N.C_2H_5\end{array}\right.$

Ethoxypseudoisatin-ethoxime.

This first yields isatin by reduction and oxidation (as does isatoxime and its two ethers, loc. cit.). The same treatment applied to ethoxy-pseudo-isatin-ethoxime yields ethylpseudoisatin,  $C_6H_4\left\langle\begin{array}{l}CO.CO\\N(C_2H_5)\end{array}\right.$ (see above). The reduction of ethyl-pseudo-isatin-ethoxime with ammonium sulphide produces diethyl indigo, in which the two ethyl groups are united to nitrogen (*Berichte*, 16, 2201):—


$$2C_6H_4\left\langle\begin{array}{l}CO.CO\\N(C_2H_5)\end{array}\right. + 2H_2 = C_6H_4\left\langle\begin{array}{l}CO.C=\!=\!=C.CO\\N(C_2H_5)(C_2H_5)N\end{array}\right\rangle C_6H_4 + 2H_2O.$$

Anthroxan Aldehyde, $C_8H_5NO_2$ =  $C_6H_4\left\langle\begin{array}{l}C—CHO\\N\end{array}\right\rangle O$ (with an atomic grouping similar to that of isatogenic ester), is isomeric with isatin, and is formed when *o*-nitrophenyl glycidic acid (p. 777) is boiled with water (together with anthranil) (*Berichte*, 16, 2226). Silver oxide converts it into **anthroxanic acid**, $C_7H_4NO.CO_2H$.

INDIGO-BLUE.

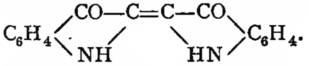
Indigo-blue or **Indigotin.** This commercially important chromogen is found in ordinary indigo and possesses the molecular formula, $C_{16}H_{10}N_2O_2$, which is in accord with its vapor density. The innumerable synthetic methods for its production, already mentioned, were discovered by A. von Baeyer. The most important of these are: the reduction of isatin chloride (p. 836) first with phosphorus (1870), then with zinc dust or HI (1879); the transformation of *o*-nitrophenyl propiolic acid (p. 815) by digestion with alkalies and reducing agents (1880); the condensation of *o*-nitrobenzaldehyde with acetone in alkaline solution (pp. 719 and 730), acetaldehyde and pyroracemic acid (p. 815) (1882); and the conversion of *a*-dibrom-*o*-nitro-acetophenone (p. 728) by boiling with alkalies (1882) (*Berichte*, 17, 963).

Recently several very simple syntheses of indigo-blue have appeared:—

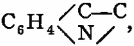
1. Fusion of bromacetanilide, $C_6H_5.NH.CO.CH_2Br$, with caustic potash, and oxidation of the aqueous solution of the product by air. The indoxyl or pseudo-indoxyl formed at first is then oxidized to indigo blue (Flimm, *Berichte*, 23, 57).

2. Indigo can also be formed by fusing phenylglycocoll, $C_6H_6.NH.CH_2.CO_2H$, with potassium hydroxide, etc., as well as from anthranilic acid (Heumann, *Berichte*, 23, 3043, 3431; Biedermann, *Berichte*, 23, 3289).

According to A. von Baeyer's investigations the constitution of indigo blue is very probably expressed by the formula:—

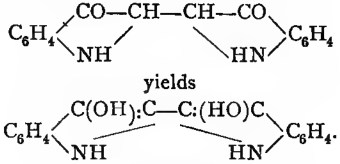


This accounts best for its entire deportment and all its transformations.

According to this formula indigo-blue contains two indol groups, , in combination with each other. That the union is through the carbon atoms follows from the synthesis of indigo-blue from *o*-dinitro-diphenyl-diacetylene (p. 802) and, therefore, diphenyl-diacetylene, $C_6H_5.C⋮C.C⋮C.C_6H_6$, may be looked upon as the parent hydrocarbon of indigo-blue. This we infer also from the formation of indigo-blue from the indoxyl and isatogenic derivatives, which is analogous to that of the indogenides (p. 833). As arguments for the existence of the group, , we have the production of indigo-blue from isatin chloride and the isatin ethers (p. 836), as well as from brom-acetophenones (see above); from the indoxyl compounds, from indoxanthic ester and di-isatogen (p. 834). Another support for this view is the fact that only those derivatives of *o*-nitro-cinnamic acid, $C_6H_4(NO_2).CH:CH.CO_2H$, yield indigo in which the carbon atom joined to the benzene nucleus is also in connection with hydroxyl or oxygen; thus the *o*-nitro-phenyl-oxyacrylic acids (p. 777) and not the *o*-nitro-cinnamic acid yield indigo. The condensation products of *o*-nitrobenzaldehyde behave similarly; *o*-nitrophenyl-lactic methyl ketone, $C_6H_4(NO_2).CH(OH).CH_2.CO.CH_3$, yields indigo, but *o*-nitro-cinnamyl-methyl ketone (p. 806) does not. With the latter bodies (in the formation of indigo-blue) there occurs a splitting-off of the excessive carbon atoms of the side-chains in the form of formic acid, acetic acid, etc.

Finally, the presence of 2 NH groups in indigo-blue is rendered very probable by the formation of di-ethyl indigo from ethyl pseudo-isatoxime (p. 837).

In the production of indigo-blue from indoxyl derivatives there occurs, in all probability, a conversion of indoxyl into pseudo-indoxyl and pseudo-isatin, and this leads us to regard indigo-blue as a *di-indogen*, corresponding to the indogenides of benzaldehydes, etc. (p. 833). The absorption of two hydrogen atoms reduces indigo-blue to *indigo-white*, $C_{16}H_{12}N_2O_2$, which has the character of a phenol. In this reaction the doubly united carbon atoms are at first saturated and then the indogen group is changed to the indoxyl group:—



Indigo-white.

Indigo-blue constitutes the principal ingredient of commercial **Indigo**, derived from different *Indigoferæ* and from woad (*Isatis tinctoria*). It occurs in these plants as a glucoside, called *indican*, which parts with its variety of glucose and becomes indigo-blue, when boiled with dilute acids, or if acted upon with a ferment (if the various portions of the plant be covered with water and exposed to the action of the air). The indigo-blue separates in the form of a powder.

Commercial indigo is a mixture of several substances, of which the indigo-blue is alone valuable. Boiling acetic acid extracts *indigo gluten* from it; and dilute potassium hydroxide takes out *indigo-brown*, which is precipitated as a brown mass by sulphuric acid. The residue finally yields to boiling alcohol the *indigo-red*, a red powder which dissolves in alcohol and ether with this color. The residual mass is almost pure indigo-blue.

Indigo-blue can be obtained from commercial indigo by sublimation, but it nearly all decomposes by the operation. It is advisable to first reduce indigo to soluble indigo-white, which can then be oxidized to indigo-blue by the exposure of the alkaline solution to the air.

Grape sugar is the best reducing agent for indigo. The latter, in a finely divided state, is mixed with an equal weight of grape sugar, and upon this are poured 1½ parts concentrated caustic soda and hot alcohol or water (150 parts), and the whole allowed to stand in a closed flask filled with the same liquid for some hours. The clear yellow solution is next poured into dilute hydrochloric acid and shaken with air (*Annalen*, 195, 305).

Indigo-blue or indigotin is a dark-blue powder with a reddish glimmer; it becomes metallic and copper-like under pressure. It sublimes in copper-red, metallic, shining prisms. It is insoluble in water, alcohol and ether, in alkalies and dilute acids, and is odorless and tasteless. It dissolves in hot aniline with a blue, in molten paraffin with a purple-red color, and can be crystallized from these solvents. It crystallizes from hot oil of turpentine in beautiful blue plates. At 300° it is converted into a dark-red vapor. If boiled with potassium hydroxide and manganese peroxide, it yields anthranilic acid (p. 748); aniline results on distilling with potassium hydroxide. See *Berichte*, 18, 1426, for the absorption spectrum of indigo and its derivatives.

We will yet mention some of the substituted indigotins, which are quite similar to indigotin and have been prepared synthetically.

Dichlor, brom-, nitro-indigoes result from the substituted isatins (p. 836), and from brom *o*-nitroacetophenones (p. 838). A *dichlor-indigo* has been prepared from *o*-nitro-*m*-chlorbenzaldehyde (*Berichte*, 18, Ref. 8). **Tetrachlor-indigo** is obtained from *o*-nitro-dichlor-benzaldehyde (*Berichte*, 18, Ref. 470). **Dimethyl indigoes** result from nitro-*m*-toluic aldehyde (p. 721) and *p*-methyl-isatin (p. 836). **Diethyl indigo** (its imide groups contain ethyl) is obtained from ethyl-pseudo-isatin-ethoxime (p. 837). **Di-isopropyl indigo, cumin indigo,** is derived from *o*-nitro-cumenyl propiolic acid (*Berichte*, 19, 261). Indigo-dicarboxylic acid, $C_{16}H_6N_2O_2(CO_2H)_2$, may be prepared from nitro-phenylpropiolic acid. It dissolves in alkalies with a bluish green color (*Berichte*, 18, 950).

The isomerides of indgotin are **indigo-red,** present in commercial indigo, **indirubin,** the indogenide of pseudoisatin (p. 833), **indigo-purpurin,** formed together with indigotin from isatin chloride (p. 836) and **indin.** The latter is obtained by the action of alcoholic potassium hydroxide upon isatid (p. 835), or by boiling dioxindol with glycerol. **Di-isatogen,** $C_{16}H_8N_2O_4$, and **indoïn** (p. 834) bear a close relation to indigotin.

Indigo White, $C_{16}H_{12}N_2O_2$, is obtained by the reduction of indigo-blue (see above). It can be precipitated from its alkaline solution by hydrochloric acid (air being excluded) as a white crystalline powder, soluble in alcohol, ether and the alkalies, with a yellowish color. It rapidly re-oxidizes to indigo-blue by exposure to the air. It yields di-indol when heated with baryta-water and zinc dust.

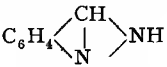
When indigo-blue is dissolved in concentrated sulphuric acid (8–15 parts) and digested for some time, we get *indigotin monosulphonic acid,* $C_{16}H_9N_2O_2.SO_3H$ (phœnicin sulphuric acid), and *indigotin disulphonic acid,* $C_{16}H_8N_2O_2(SO_3H)_2$ (cœrulin sulphuric acid). Water precipitates the former from its solution as a blue powder, soluble in pure water and alcohol, but not in dilute acids. Its salts with the bases possess a purple-red color and dissolve with a blue color in water.

The disulphonic acid is obtained when indigo is digested with strong, fuming sulphuric acid. It can be absorbed from its aqueous solution by clean wool and again removed from the latter by ammonium carbonate. Its alkali salts, *e. g.*, $C_{16}H_8N_2O_2(SO_3K)_2$, are sparingly soluble in salt solutions, and are thrown out from their solution in the form of dark-blue precipitates by alkaline carbonates and acetates. They constitute in commerce what is known as *indigo-carmine.* When the indigotin sulphonic acids are reduced, they yield, just as does indigo-blue, the indigo-white sulphonic acids.

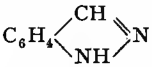
Goods (wool) are dyed in two ways with indigo: the wool is immersed in the aqueous solution of indigotin sulphonic acid (Saxony-blue dyeing), or the indigo-blue is changed by fermentation to indigo-white (indigo-vat), the cloth saturated with the latter and exposed to the air, when indigo-blue forms and sets itself upon the fibre. In printing, a mixture of *o*-nitrophenyl propiolic acid and an alkaline reducing agent (potassium xanthate, etc.) are sometimes substituted for the indigo. Steaming causes the formation of indigo-blue.

4. BENZO-AZOLE COMPOUNDS.

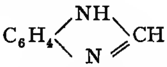
The benzoazoles or benzodiazoles attach themselves to indol or benzopyrrol (p. 826). They contain a "five-membered ring" with two nitrogen atoms (p. 551). Like the azole derivatives they occur as *α*- or (1, 2)-diazoles (with two adjacent *n*-atoms) and as *β*- or (1, 3)-diazoles. The first are known in two forms, *indazoles* and *isindazoles* (benzopyrazoles). The *β*-benzodiazoles contain (in addition to the benzene ring) the ring of glyoxaline (p. 551); hence they may be termed *Benzoglyoxalines* (*Annalen*, 227, 303; *Berichte*, 18, Ref. 223):—



α-Benzodiazole,
Indazole.

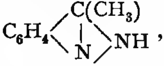


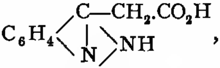
Benzopyrazole,
Isindazole.



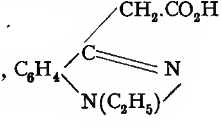
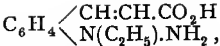
β-Benzodiazole,
Benzoglyoxaline.

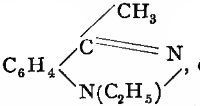
(1) **Indazole**, $C_7H_6N_2$, is formed by heating *o*-hydrazine-cinnamic acid,  $C_6H_4\begin{cases}CH{:}CH.CO_2H\\NH.NH_2\end{cases}$, when acetic acid is eliminated. It crystallizes from hot water in colorless needles, melting at 146°, and boiling at 270°. It is soluble in dilute acids. Its salts are very unstable. It yields *n*-ethyl indazole, $C_7H_5N_2(C_2H_5)$, when it is heated with ethyl iodide.

α-**Methyl Indazole**, , is derived from *o*-hydrazine-acetophenone,  $C_6H_4\begin{cases}CO.CH_3\\NH.NH_2\end{cases}$. It melts at 113° and boils at 280°.

α-**Indazole Acetic Acid**, , results from the oxidation of *o*-hydrocinnamic acid, in alkaline solution, on exposure to the air. It crystallizes from hot water in yellow needles, melting at 168–170°, decomposing at the same time into carbon dioxide and *α*-methyl indazole.

(2) *Isindazole or Benzo-pyrazole* compounds (see above) were formerly considered to be quinazole derivatives (they contain a side-chain of six members). **Isindazole**, $C_7H_6N_2$, the parent substance, is only known in its derivatives.

n-**Ethyl-isindazole Acetic Acid**, , is formed when the aqueous solution of ethyl hydrazine-cinnamic acid,  $C_6H_4\left\langle\begin{matrix}CH{:}CH.CO_2H\\ N(C_2H_5).NH_2\end{matrix}\right.$, is shaken with air. It melts at 131°, and at 162° breaks down into carbon dioxide and ethyl-methyl isindazole.

n-**Ethyl-methyl Isindazole**, , called ethyl quinazole, is derived from nitrosoethyl-*o*-amidoacetophenone,  $C_6H_4\left\langle\begin{matrix}CO.CH_3\\ N(C_2H_5).NO\end{matrix}\right.$. A yellow oil, that solidifies in the cold to a leafy mass, melting at 30°. It forms salts with acids; much water, however, decomposes them (*Berichte*, 18, Ref. 227).

There is a compound formed by the condensation of the product resulting from the action of diazobenzene chloride upon dinitro-phenylacetic ester (*Berichte*, 22, 321; 23, 714), that should probably be included among the isindazole derivatives.

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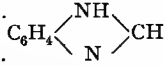
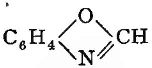
(3) *Benzo-glyoxaline* compounds (see above), condensation products of the *o*-phenylene diamines, have been described with the latter, and there designated as *anhydrobases* or *aldehydines* (p. 627).

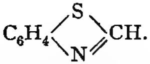
Benzo-glyoxaline, $C_7H_6N_2$ = , is ordinarily known as *phenylene methenyl amidine* (p. 628).

(4) We may yet add to the benzo-diazoles (or imidazoles) the *benzo-oxazoles* and *benzo-thiazoles*. These not only contain the benzene-ring but also those of oxazole and thiazole (pp. 554, 555):—



Benzo-oxazole
Methenylamidophenol.

and



Benzthiazole,
Methenylamidothiophenol.

They have been obtained as condensation products of *o*-amidophenol and *o*-amidothiophenol, hence are usually treated with these (p. 679).

DERIVATIVES WITH TWO OR MORE BENZENE NUCLEI.

Although in general very stable the benzenes yet possess to a high degree the power, by exit of hydrogen, of combining with each other in part directly, and partly by the assistance of other carbon atoms. The hydrocarbons derived in this manner yield numerous derivatives.

They may be classified as follows: (1) those with directly combined benzene nuclei, *diphenyl* derivatives; (2) those in which the benzene nuclei are joined by 1 carbon atom, *di-* and *triphenyl methane* derivatives; (3) those with benzene nuclei linked together by two or more carbon atoms, *dibenzyl* derivatives; (4) those with condensed benzene nuclei, *naphthalene* and *anthracene* derivatives.

1. Derivatives of directly combined benzene nuclei.

DIPHENYL GROUP.*

(1) **Diphenyl,** $C_{12}H_{10} = C_6H_5.C_6H_5$, results from the action of sodium upon the solution of brom-benzene in ether or benzene: $2C_6H_5Br + Na_2 = C_{12}H_{10} + 2NaBr$. It is also produced in slight amount when benzoic acid is distilled with lime (together with traces of benzene). It is present in that portion of coal-tar which boils about 240–260°.

Preparation.—Conduct benzene vapors through an iron tube heated to redness. The tube is filled with fragments of pumice stone. The yield of the diphenyl is about 50 per cent. of the benzene taken (*Berichte*, 10, 1602). It may be obtained from aniline by converting the latter into diazobenzene sulphate and decomposing the latter with copper or zinc dust (p. 634) (*Berichte*, 23, 1226).

Diphenyl crystallizes from alcohol and ether in large, colorless leaflets, melting at 71°, and boiling at 254°. If dissolved in glacial acetic acid and oxidized with chromic anhydride it yields benzoic acid.

Metallic sodium reduces diphenyl, dissolved in amyl alcohol, to *tetra-hydro-diphenyl*, $C_{12}H_{14}$, boiling at 245°. The latter readily forms a dibromide which alcoholic potash converts into *dihydro-diphenyl*, $C_{12}H_{12}$, boiling at 248° (*Berichte*, 21, 846).

The halogens, nitric acid and sulphuric acid convert diphenyl into *mono-* and *di-substitution products*. In the first, *e.g.*, $C_{12}H_9Br$, $C_{12}H_9(NO_2)$, $C_{12}H_9SO_3H$, the substitution groups occupy the para-position, referred to the point of union of the two benzene nuclei. When these are oxidized with chromic acid we obtain para-derivatives of benzoic acid, the other benzene nucleus being destroyed. The di-derivatives, *e.g.*, $C_{12}H_8Br_2$, occur in two isomeric modifications. The di-para-derivatives predominate; in these the two side-chains have the para-position referred to the point of union. Chromic acid oxidizes them to two para-derivatives of benzoic acid; thus from brom-nitro diphenyl we get para-brom and para-nitro-benzoic acid.

The energetic chlorination of diphenyl and its derivatives (p. 580), produces *perchlor-diphenyl*, $C_{12}Cl_{10}$; brilliant plates or prisms, melting above 280°, and boiling at about 440°. Like perchlor-benzene, it is very stable, and does not undergo any further decomposition.

The nitration of diphenyl in the cold, or when dissolved in glacial acetic acid, yields two nitro diphenyls, $C_{12}H_9(NO_2)$; the para-compound is not soluble in alcohol, melts at 113°, boils at 340°, and when oxidized with chromic acid becomes para-nitro-benzoic acid. The other nitro-diphenyl (very probably ortho) forms plates, melting at 37° and boiling at 320°.

Fuming nitric acid produces α- and β-dinitro-diphenyl, $C_{12}H_8(NO_2)_2$; the former (dipara) is very sparingly soluble in hot alcohol, and melts at 233°, and by reduction yields diphenylin. The dimeta-compound, from dinitro-benzidine, melts at 197°.

(2) **Phenyl Tolyls,** $C_6H_5.C_6H_4.CH_3$, *Methyl Diphenyls.* The para-compound, like diphenyl, results from the action of sodium upon a mixture of brombenzene

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[*] Consult *Annalen*, 207, 363, for a tabulation of these diphenyl derivatives.

and *p*-bromtoluene. A liquid boiling at 265°, and solidifying below 0°. Its sp. gr. is 1.015. Chromic acid oxidizes it to *p* diphenyl carboxylic acid and terephthalic acid.

(3) **Ditolyls,** $CH_3.C_6H_4.C_6H_4 CH_3$, dimethyl diphenyls. The di-para-compound is produced by the action of sodium upon *p*-bromtoluene. It melts at 121° and distils without decomposition. It yields *pp*-diphenyl dicarboxylic acid (p. 850) when oxidized. *mm*-Ditolyl has been obtained from *o*-tolidine by the substitution of the two NH_2-groups. It is an oil boiling at 289° (*Berichte*, 21, 1096).

Amido-derivatives.

Amido-diphenyls, $C_6H_5.C_6H_5.NH_2$. The *ortho* compound, from *o*-nitrodiphenyl, melts at 45°. The *para* compound, xenylamine, crystallizes from hot water in colorless leaflets, melts at 49° and boils at 322°.

1. **Diamido-diphenyl,** $C_{12}H_8(NH_2)_2$. (1) (di-para), **Benzidine** (4,4) is obtained: by the reduction of *pp*-dinitrodiphenyl; and by the action of sodium upon para-brom-aniline. It is technically prepared from azobenzene by the action of tin and hydrochloric acid upon its alcoholic solution (*Annalen*, 207, 330); the hydrazobenzene formed at first rearranges itself to benzidine (p. 649) (compare *Berichte*, 23, 3265). In the cold the latter is the chief product. Diphenylin is also formed on the application of heat:—

$$C_6H_5.NH—NH.C_6H_5 \quad \text{yields} \quad H_2N.C_6H_4—C_6H_4.NH_2.$$

Benzidine dissolves easily in hot water and alcohol, crystallizes in silvery leaflets melting at 122°, and subliming with partial decomposition. It forms salts with two equivalents of acid; the sulphate,

$$C_{12}H_6(NH_2)_2.SO_4H_2,$$

is almost wholly insoluble in water. It oxidizes to quinone if boiled with manganese dioxide and dilute sulphuric acid.

Consult *Berichte*, 23, Ref. 644, for the compounds of benzidine with aldehydes.

oo-**Dinitrobenzidine,** $C_{12}H_6(NO_2)_2(NH_2)_2(NH_2:NO_2 = 4:3)$, * (is formed on nitrating diacetobenzidine. Red crystals, melting at 220°. When the two NH_2-groups are substituted it forms *mm*-dinitrodiphenyl) (p. 843). $SnCl_2$ reduces it to *oo*-diamidobenzidine.

The nitration of benzidine in concentrated sulphuric acid gives rise to *mm*-**Dinitrobenzidine,** $C_{12}H_6(NO_2)_2(NH_2)_2(NH_2:NO_2 = 4.2)$, crystallizing in yellow leaflets, melting at 214° (*Berichte*, 23, 795). When reduced it yields *mm-diamido-benzidine* (leaflets melting at 165°), which loses NH_3 and forms diamidocarbazol, $C_{12}H_6(NH_2)_2:NH$ (p. 847) (*Berichte*, 23, 3252).

When benzidine is heated with concentrated sulphuric acid (2 parts) to 210° (*Berichte*, 22, 2464) it becomes *oo*-**Benzidine-disulphonic Acid,** $C_{12}H_6(NH_2)_2(SO_3H)_2(NH_2:SO_3H = 4:3)$; its diazo-derivatives are feeble dye-stuffs.

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* The terms *o*- and *m*- with the benzidine derivatives refer to the amido-groups; in the case of diphenyl to the points of union (p. 843) (*Berichte*, 23, 3268).

mm-**Benzidine Disulphonic Acid** (NH_2:SO_3H = 4 : 2) is prepared by the reduction of an alkaline solution of *m*-nitro-benzene sulphonic acid and its further transposition (*Berichte*, 22, Ref. 785). It does not yield dye-substances; they may be obtained from the diamido-diphenylene oxide $(H_2N.C_6H_3)_2O$, prepared by fusing it with caustic potash. **Benzidine Sulphone,** $C_{12}H_6(NH_2)_2SO_2$, is prepared by heating benzidine sulphate with fuming sulphuric acid (*Berichte* 21, Ref. 873; 22, 2467).

pp-**Oxyamido-diphenyl,** $H_2N.C_6H_4.C_6H_4.OH$, is formed by replacing the NH_2-group of benzidine by hydroxyl. It yields a yellow color with salicylic acid and a reddish violet with 1-naphthol-4-sulphonic acid.

2. *mm* - **Diamido - diphenyl,** $H_2N.C_6H_4.C_6H_4.NH_2(C_2{:}NH_2 = 1:3)$, is formed when eliminating the two NH_2-groups from *oo*-dinitrobenzidine (see above).

3. *op*-**Diamido-diphenyl, Diphenylin,** is obtained, together with benzidine, by the rearrangement of hydrohenzene or by the reduction of azobenzene with tin and hydrochloric acid. It crystallizes in needles, melting at 45° and boils at 232°. See *Berichte*, 22, 3011, for its derivatives.

2. **Diamido-phenyl-tolyl,** $H_2N.C_6H_4.C_6H_3(CH_3).NH_2(CH_3{:}NH_2 = 4:3)$, *o*-Methyl Benzidine, is formed upon reducing a mixture of nitrobenzene and *o*-nitrotoluene in alkaline solution. It melts at 115° and yields substantive dyestuffs (*Berichte*, 23, 3222).

3. **Diamido-ditolyls, Tolidines,** $H_2N.C_6H_3(CH_3).C_6H_3(CH_3).NH_2$. They are produced, like benzidine, by the alkaline reduction of the three nitrotoluenes and further rearrangement of the resulting hydrazotoluenes. In doing this the two benzene rings, in *o*- and *m*-tolidine (from *o*- and *m*-nitrotoluene) unite at the para-points, with reference to the amido-groups; in the case of *p*-tolidine (from *p*-nitrotoluene) they combine at the ortho-positions. The first two contain the $2NH_2$-groups in para-positions relative to the diphenyl union, hence yield substantive azo-dyes (see below) (see *Berichte*, 21, 3145). The substituted azobenzenes (*Berichte*, 23, 3265) deport themselves similarly.

o-*Tolidine*, from *o*-nitrotoluene (see above), crystallizes in leaflets with mother-of-pearl lustre, and melting at 128° (*Berichte*, 21, 746, 1065). It is largely used in the manufacture of substantive azo-dyes. See *Berichte*, 21, Ref. 874; 22, 2473 for the sulpho-acids of *o*-tolidine.

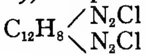
m-*Tolidine*, from *m*-nitrotoluene (*Berichte*, 22, 838), separates from its salts as an oil, which gradually solidifies and melts at 109°.

p-*Tolidine*, from *p*-azotoluene (*Berichte*, 17, 472), forms delicate leaflets, melting at 103°.

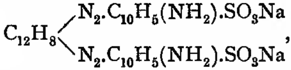
Ditolylin, $H_2N.C_7H_6.C_7H_6.NH_2$ (corresponding to diphenylin, see above), is formed together with *o*-tolidine (see above), and does not yield substantive dyes (*Berichte*, 23, 3253).

Analogous diamidodiphenyls have been prepared from nitroxylenes (*Berichte*, 21, 3147).

Benzidine Dyes.

By diazotizing benzidine (action of sodium nitrite (2 molecules) and hydrochloric acid upon its salts, p. 629) we produce the salts of tetrazo- or bis-diazodiphenyl, *e. g.*,  $C_{12}H_8\left\langle\begin{matrix}N_2Cl\\N_2Cl\end{matrix}\right.$ (p. 639);

these combine with amines and phenols (amine sulpho-acids, phenol sulpho-acids, oxycarboxylic acids, etc.) forming disazo-or tetrazo-compounds (pp. 645–652). These azo dyes possess the remarkable property of fixing themselves in the form of alkali salts upon unmordanted plant fibres (P. Griess, 1879; *Berichte*, **22**, 2459). They are called *substantive dyes* (cotton dyes), and are largely employed in dyeing. Diphenyl tetrazochloride and salicylic acid yield a yellow dye, whose sodium salt, $C_{12}H_8[N_2.C_6H_3(OH).CO_2Na]_2$ is *chrysamine* or *flavophenine* (the first benzidine dye applied technically) (*Berichte*, **22**, 2459). Diphenyl-tetrazo-chloride and α-naphthylamine sulphonic acid (naphtionic acid) (2 molecules) form a red dye; its sodium salt is the technically important *Congo red* (Böttger, 1884):—



$$C_{12}H_8\begin{cases}N_2.C_{10}H_5(NH_2).SO_3Na\\N_2.C_{10}H_5(NH_2).SO_3Na\end{cases}$$

, Congo Red.

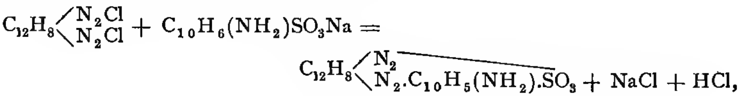
All the substantive dyestuffs, similar to benzidine, yield diamido-diphenyls and analogous bodies, containing the two diamido-groups in the para position with reference to the diphenyl union, *e. g.*, orthotolidine (p. 845), diamidostilbene, $H_2N.C_6H_4.CH:CH.C_6H_4.NH_2$ (*Berichte*, 21, Ref. 383), dimethyl oxybenzidine (p. 848); further, thiotoluidines (p. 684), thiobenzidine, etc. (*Berichte*, 20, Ref. 272). It may be said that *as a rule* those *substituted* benzidines (nitro and sulpho-benzidines, tolidines, etc.) having the substitution in the meta-position (relative to the amido-group) yield *inactive*, or *feeble substantive* azo dyes. Diamido-diphenylene oxide, benzidine sulphone (p. 845) and diamido carbazol (p. 847) constitute exceptions. They contain a third ring-shaped chain (*Berichte*, 23, 3252, 3268).

The *o*-tolidine derivatives are also important from a practical standpoint. Thus, *o*-tolidinetetrazochloride and α- and β-naphthylamine sulphonic acids yield two *benzopurpurines*, that form blue-tinted red; α-naphthol-sulphonic acid forms the red-tinted blue dye—*azoblue*, $C_{12}H_6(CH_3)_2[N_2.C_{10}H_5.(OH).SO_3Na]_2$ (*Berichte*, 19, Ref. 422). Dimethoxyl-benzidine (dianisidine) (p. 836) and α-naphtholsulphonic acid form the blue *benzazurine*, stable on exposure to the light. More recent dyes are *sulphon-azurine*, from benzidine sulphone (p. 845) (*Berichte*, 22, 2499), and various dyestuffs from diamido diphenylene oxide (p. 846) (*Berichte*, 23, Ref. 442).

For the preparation of these dye-substances add the aqueous solution of the tetrazochloride to the aqueous solution of two molecules of the sodium salt of the other component:—

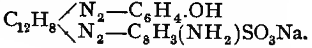
$$C_{12}H_8(N_2Cl)_2 + 2C_{10}H_6(NH_2)SO_3Na =$$
$$C_{12}H_8(N_2.C_{10}H_5(NH_2).SO_3NO)_2 + 2HCl.$$

Sodium acetate, sodium carbonate or ammonia is added to the solution of the sodium salt to combine the hydrochloric acid which is liberated. In all these reactions the tetrazochloride first acts upon but one molecule of the amine or phenol, forming an immediate product that dissolves with difficulty, as—



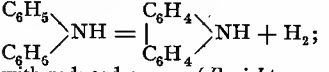
$$C_{12}H_8\begin{cases}N_2Cl\\N_2Cl\end{cases} + C_{10}H_6(NH_2)SO_3Na =$$
$$C_{12}H_8\begin{cases}\overline{N_2\qquad\qquad\qquad\quad}\\N_2.C_{10}H_5(NH_2).SO_3\end{cases} + NaCl + HCl,$$

which immediately, in alkaline solution, attacks the second molecule of the amine or phenol. If the intermediate product be allowed to act upon a different amine or phenol *mixed* tetrazodyes (see *Berichte*, 19, 1697, 1755; 21, Ref. 71) result. Diphenyltetrazo-chloride, sulphanilic acid (1 molecule) and phenol (1 molecule) yield a mixed dye of this description:—

Congo yellow = 

$$C_{12}H_8\left\langle\begin{matrix}N_2-C_6H_4.OH\\N_2-C_8H_3(NH_2)SO_3Na.\end{matrix}\right.$$

Diphenylimide, Carbazol, $C_{12}H_9N$, is produced when the vapors of diphenylamine or aniline are conducted through a tube heated to redness:—



$$\begin{matrix}C_6H_5\\C_6H_5\end{matrix}\Big\rangle NH = \begin{matrix}C_6H_4\\|\\C_6H_4\end{matrix}\Big\rangle NH + H_2;$$

also upon heating thiodiphenylamine (p. 604) with reduced copper (*Berichte*, 20, 233).

It occurs in that portion of crude anthracene boiling at 320–360°, and is a by-product in the manufacture of aniline. Carbazol dissolves in hot alcohol, ether and benzene, crystallizes in colorless leaflets, melts at 238° and distils at 351°. Its concentrated sulphuric acid solution has a yellow color, and is colored a dark green by oxidizing agents. The nitrogen atom of diphenylimide is inserted in the two ortho-positions of the two benzene rings (relatively to the diphenyl union); with two carbon atoms of each of these nuclei it forms a *closed, five-membered ring*, such as is present in pyrrol and in indol (*Berichte*, 20, 234). This explains the similarity of many reactions of carbazol with those of pyrrol and indol (*Berichte*, 21, 3299). Thus, it gives the pine shaving reaction, the dark blue coloration with sulphuric acid and isatin, and forms with nitric acid a compound that crystallizes in red needles, melting at 186°. Its *acetate*, $C_{12}H_8N.C_2H_3O$, melts at 69°. Its *nitroso-derivative*, $C_{12}H_8.N.NO$, consists of long, golden yellow needles, melting at 82°. A dye, analogous to diphenylamine blue, is produced upon heating together carbazol and oxalic acid (*Berichte*, 20, 1904). *pp*-Diamido-carbazol, $C_{12}H_7(NH_2)_2N$, is formed when *mm*-diamido-benzidine (p. 845) is heated to 180° with hydrochloric acid. It forms needles with a silvery lustre. It chars above 200°. Its tetrazo-compounds form substantive dyes (*Berichte*, 23, 3267). See *Berichte*, 22, 2185 for *tetra hydro-carbazol*, $C_{12}H_{13}N$. **Phenyl-naphthyl carbazol,** $C_{16}H_{13}N = \left\langle\begin{matrix}C_8H_4\\C_{10}H_8\end{matrix}\right\rangle NH$, is perfectly analogous to carbazol. It is found in the anthracene residues, and is prepared artificially from β-phenyl-naphthylamine, $C_{10}H_9.NH.C_6H_5$. It is greenish-yellow in color and melts at 330°.

Azo-diphenylene, $\left\langle\begin{matrix}C_6H_4\\C_6H_4\end{matrix}\right\rangle N_2$, is produced when the calcium azobenzoates (ortho-, meta-, para) are distilled. It sublimes in yellow needles, melting at 170°.

We obtain a mono- and a di-sulphonic acid, $C_{12}H_9.SO_3H$, and $C_{12}H_8(SO_3H)_2$, on digesting diphenyl with sulphuric acid. The first is formed with a very little sulphuric acid. The disulpho-acid (di-para) crystallizes in deliquescent prisms, melting at 72.5°. The oxy-diphenyls are the products on fusion with alkalies.

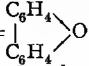
Oxy-diphenyl, $C_{12}H_9.OH$, Diphenylol, is obtained by diazotizing amidodiphenyl sulphate. It sublimes in shining leaflets, melting at 165°. It boils at 305–308°. It dissolves with a beautiful green color in concentrated sulphuric acid.

Dioxydiphenyls, *Diphenols*, $C_{12}H_8(OH)_2$. The di-para-compound, $C_6H_4(OH).C_6H_4(OH)(\gamma)$, is obtained from benzidine by means of the diazo-compound and by fusing diphenyl-disulphonic acid with caustic alkali. It consists of shining leaflets or needles, melting at 272° and boiling above 360°. *po*-Diphenol (δ), formed on fusing phenol-ortho- and para-sulphonic acids with potassium hydroxide, and from diphenylin, through the diazo-compound, melts at 161°. Two additional diphenols (α and β) are obtained when phenol is fused with caustic potash; the α-melts at 123° and the β- at 190°.

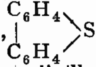
Oxydiphenyl-amido-derivatives can be produced by nitrating and reducing the oxydiphenyls (*Berichte*, 21, 3331; 22, 335), or from the oxyazobenzenes by the molecular rearrangement of the hydrazo-compounds formed at first (*Berichte*, 23, 3256):—

$$C_6H_6.N:N.C_6H_4.O.CH_3 \text{ yields } H_2N.C_6H_4.C_6H_3(O.CH_3).NH_2.$$

The arrangement does not occur unless a para position of the benzene nuclei is unoccupied (*Berichte*, 23, 3256). Various diamido diphenol ethers (*e. g.*, dimethoxyl-benzidine from nitranisol) form blue dyestuffs, like *benzoazurine* (p. 846) (*Berichte*, 21, Ref. 872) with naphthol sulphonic acid.



Diphenylene Oxide, $C_{12}H_8O = \begin{matrix} C_6H_4 \\ | \\ C_6H_4 \end{matrix} \!\!\!\!\!\!\begin{matrix} \diagdown \\ \\ \diagup \end{matrix}\!\! O$, results when phenylphosphate is distilled with lime, or from calcium phenylate or phenol and lead oxide under the same treatment. It crystallizes in leaflets melting at 81° and distilling at 287°.



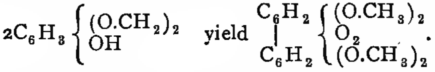
Diphenylene Sulphide, $\begin{matrix} C_6H_4 \\ | \\ C_6H_4 \end{matrix} \!\!\!\!\!\!\begin{matrix} \diagdown \\ \\ \diagup \end{matrix}\!\! S$, is produced when phenyl sulphide and phenyl disulphide (p. 672) are distilled through an ignited tube. Shining needles or leaflets, melting at 97° and distilling at 332°. Chromic acid oxidizes it to diphenylene sulphone, $C_{12}H_8:SO_2$.

Coeroulignone or **Cedriret**, $C_{16}H_{16}O_6$, is a derivative of hexa-oxydiphenyl:—

$$C_{12}H_4\left\{\begin{matrix}(O.CH_3)_4 \\ O_2.\end{matrix}\right. \qquad C_{12}H_4\left\{\begin{matrix}(O.CH_3)_4 \\ (OH)_2\end{matrix}\right. \qquad C_{12}H_4(OH)_6.$$

Coerouliguone. Hydrocoeroulignone. Hexa-oxy-diphenyl.

Coeroulignone separates as a violet powder when crude wood-spirit is purified on a large scale by means of potassium chromate. It is further formed on oxidizing dimethyl-pyrogallol (p. 695) with potassium chromate or ferric chloride:—



$$2C_6H_3\left\{\begin{matrix}(O.CH_3)_2 \\ OH\end{matrix}\right. \text{ yield } \begin{matrix} C_6H_2 \\ | \\ C_6H_2 \end{matrix}\left\{\begin{matrix}(O.CH_3)_2 \\ O_2 \\ (O.CH_3)_2\end{matrix}\right. .$$

Coerulignone is insoluble in the ordinary solvents, and is precipitated in fine, steel-blue needles, from its phenol solution, by alcohol or ether. It dissolves in concentrated sulphuric acid with a beautiful blue color, resembling that of the corn-flower. Large quantities of water color the solution red at first. Reducing agents (tin and hydrochloric acid) convert coeroulignone into colorless hydrocoeroulignone, which changes again to the first by oxidation. Coeroulignone is, therefore, a quinone body, deports itself towards hydrocoeroulignone like quinone to hydroquinone, and hence may be called a double-nuclei quinone (p. 698).

Hydrocoeroulignone, $C_{16}H_{16}O_6$, crystallizes from alcohol and glacial acetic acid in colorless leaflets, melting at 190°, and distils with almost no decomposition. It is a divalent phenol. When heated with concentrated hydrochloric or hydriodic acid it breaks up into methyl chloride and **Hexaoxydiphenyl,** $C_{12}H_{10}O_6$:—

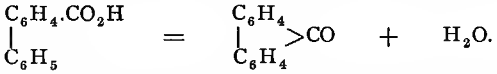
$$C_{12}H_4\left\{\begin{matrix}(O.CH_3)_4\\(OH)_2\end{matrix}\right. + 4HCl = C_{12}H_4(OH)_6 + 4CH_3Cl.$$

The latter crystallizes from water in silvery leaflets. It dissolves with a beautiful bluish-violet color in potassium hydroxide. Acetyl chloride converts it into an *hexacetate.* Diphenyl results when it is heated with zinc dust.

If potassium diphenyl-mono-sulphonate and disulphonate be distilled with potassium cyanide the *nitriles,* $C_{12}H_9.CN$ and $C_{12}H_8(CN)_2$, result; the former melts at 85°, the latter at 234°. The corresponding diphenyl-carboxylic acids are obtained when these are saponified with alcoholic potassium hydroxide or with hydrochloric acid.

Diphenyl-carboxylic Acids, $C_{13}H_{10}O_2 = C_6H_5.C_6H_4.CO_2H$. The three possible isomerides are known.

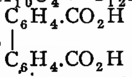
The *ortho*-acid, **o-phenyl-benzoic acid,** is produced by fusing diphenylene ketone (p. 851) with caustic potash. It dissolves with difficulty in hot water and melts at 111°. Diphenylene is reformed when it is distilled with lime. It sustains a similar change upon being heated with sulphuric acid to 100° (*Berichte,* 20, 847):—



$$\begin{matrix}C_6H_4.CO_2H\\|\\C_6H_5\end{matrix} = \begin{matrix}C_6H_4\\|\\C_6H_4\end{matrix}\!>CO + H_2O.$$

If its sodium salt be heated with $POCl_3$, the product will be diphenylene ketonoxide (p. 860). The *meta*-acid is formed by oxidizing isodiphenylbenzene and melts at 161°. The *para*- is formed from diphenyl cyanide and when *p*-diphenyl benzene (p. 852) is oxidized with CrO_3 and glacial acetic acid or phenyl tolyl with nitric acid. It crystallizes from alcohol in bundles of grouped needles, melting at 218°. It affords diphenyl on distillation with lime, and yields terephthalic acid if oxidized with a chromic acid mixture.

Diphenyl-dicarboxylic Acids, $C_{14}H_{10}O_4 = C_{12}H_8(CO_2H)_2$.

(1) The *ortho*-acid, **Diphenic Acid,**  $\begin{matrix}C_6H_4.CO_2H\\|\\C_6H_4.CO_2H\end{matrix}$ (*Berichte,* 20, 847), is produced when phenanthrene or phenanthraquinone are oxidized with a chromic acid mixture; from the latter also by the action of an alcoholic potassium hydroxide solution. It is very readily soluble in hot water, alcohol and ether, crystallizes in shining needles or leaflets, melting at 229°, and sublimes. Its barium and calcium salts are readily soluble in water. The *dimethyl ester* melts at 73°; the *diethyl ester* at 42°. Chromic acid changes diphenic acid to carbon dioxide. It yields diphenyl when distilled with soda-lime; heated with lime it forms diphenylene ketone. When diphenic acid is digested with acetic anhydride, its *anhydride,* $C_{12}H_8(CO)_2O$, is formed. This melts at 213–217°, and when heated to 120° with concentrated sulphuric acid decomposes into carbon dioxide and diphenylene ketone carboxylic acid (p. 852) (*Berichte,* 21, Ref. 726).

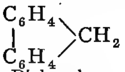
The nitration of diphenic acid produces two *dinitro-diphenic acids,* $C_{12}H_6(NO_2)_2(CO_2H)_2$, *a* and *β*, which are also formed in the oxidation of dinitro phenanthraquinone. The reduction of the *α*-acid (melting at 253°) with tin and hydrochloric acid yields *diamido-diphenic acid*, $C_{12}H_6(NH_2)_2(CO_2H)_2$, which may also be obtained through the molecular transposition of meta-hydrazo-benzoic acid (p. 751). Distilled with baryta or lime it yields benzidine (together with diamido-fluorene). The elimination of the NH_2 group causes it to change to diphenic acid. We, therefore, infer that the latter (and also Phenanthrene, see this) is a diortho-derivative of diphenyl.

(2) **Isodiphenyl Dicarboxylic Acid,** $C_6H_4(CO_2H).C_6H_4(CO_2H)$, *isodiphenic acid* (ortho-meta), may be prepared by fusing *α*-diphenylene-ketone carboxylic acid with caustic potash. It dissolves with difficulty in water and melts at 216°. Chromic acid oxidizes it to isophthalic acid. It yields diphenylene ketone when distilled with lime.

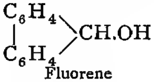
(3) *pp*-**Diphenyl-dicarboxylic Acid** is obtained from diphenyl-dicyanide, and by oxidizing ditolyl with chromic acid in a glacial acetic acid solution. It is an amorphous white powder, insoluble in alcohol and ether. It decomposes at higher temperatures without first fusing. Heated with lime it affords diphenyl.

(4) *op*-**Diphenyl Dicarboxylic Acid** may be obtained from diphenylene by replacing its amido-groups with CN and then saponifying. White crystalline leaflets, melting at 231° (*Berichte*, 22, 3019).

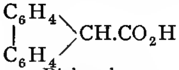
We also have a series of compounds, the *diphenylene derivatives*, in which 2 hydrogen atoms of the diphenyl group (both in the ortho-position with reference to the point of union of the diphenyl group), are replaced by one carbon atom. The following bodies are classed here:—


$\begin{array}{l} C_6H_4 \\ | \\ C_6H_4 \end{array}\!\!>CH_2$

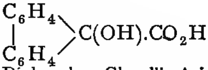
Diphenylene Methane.


$\begin{array}{l} C_6H_4 \\ | \\ C_6H_4 \end{array}\!\!>CH.OH$

Fluorene Alcohol.

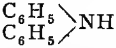

$\begin{array}{l} C_6H_4 \\ | \\ C_6H_4 \end{array}\!\!>CH.CO_2H$

Diphenylene Acetic Acid.

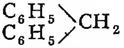

$\begin{array}{l} C_6H_4 \\ | \\ C_6H_4 \end{array}\!\!>C(OH).CO_2H$

Diphenylene Glycollic Acid.

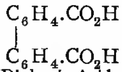
Carbazol, diphenylene oxide (p. 847) and diphenylene sulphide, are such diphenylene-diortho-derivatives. Intimately related to the diphenylene derivatives, *e. g.*,


$\begin{array}{l} C_6H_5 \\ C_6H_5 \end{array}\!\!>NH$

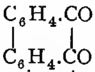
or


$\begin{array}{l} C_6H_5 \\ C_6H_5 \end{array}\!\!>CH_2$

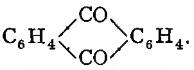
they are frequently derived from the latter on heating, by an ortho-condensation of the two phenyl groups with the exit of two hydrogen atoms. Diphenic acid, phenanthraquinone and anthraquinone are intimately related to them:—


$\begin{array}{l} C_6H_4.CO_2H \\ | \\ C_6H_4.CO_2H \end{array}$

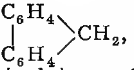
Diphenic Acid.


$\begin{array}{l} C_6H_4.CO \\ |\qquad\ \ | \\ C_6H_4.CO \end{array}$

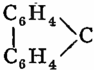
Phenanthraquinone.

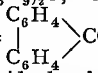

$C_6H_4\!\!<\!\!\begin{array}{c} CO \\ CO \end{array}\!\!>\!\!C_6H_4.$

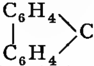
Anthraquinone.

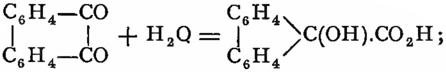
Diphenylene Methane, $C_{13}H_{10} =$  $\begin{array}{l} C_6H_4 \\ | \\ C_6H_4 \end{array}\!\!>CH_2$, **Fluorene,** occurs in coal tar (boiling at 300–305°) and is obtained by conducting diphenylmethane, $(C_6H_5)_2CH_2$, through an ignited tube, also on heating diphenylene ketone with zinc dust, or with hydriodic acid and phosphorus to 160°. (For the detection of fluorene in presence of phenanthrene and anthracene see *Berichte*, 11, 203).

It crystallizes from hot alcohol in colorless leaflets with a violet fluorescence, melts at 113°, and boils at 295°. It forms a compound with picric acid, which crystallizes in red needles, melting at 80–82°. The chromic acid mixture oxidizes it to diphenylene ketone. Fusion with caustic potash produces dioxydiphenyl.

Fluorene Alcohol,  $\begin{array}{l}C_6H_4\\ |\\ C_6H_4\end{array}\!\!>CH.OH$, results in the action of sodium amalgam upon the alcoholic solution of diphenylene ketone and by heating sodium diphenylene glycollic acid to 120°. It crystallizes from hot water in fine needles, from alcohol in six-sided plates, melting at 153°. Chromic acid changes it back to diphenylene ketone. Concentrated sulphuric acid or P_2O_5 colors it an intense blue, and produces *fluorene ether*, $(C_{13}H_9)_2O$, melting at 290°.

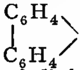
Diphenylene Ketone, $C_{13}H_8O$ =  $\begin{array}{l}C_6H_4\\ |\\ C_6H_4\end{array}\!\!>CO$, is obtained from diphenic acid, isodiphenic acid or *o*-phenylbenzoic acid when heated with lime and by oxidizing diphenylene-methane with a chromic acid mixture, and by heating anthraquinone and phenanthraquinone with caustic lime (*Annalen*, 196, 45). It is very soluble in alcohol and ether, crystallizes in large yellow prisms, melting at 84°, and boiling at 337°. Being a ketone it unites with hydroxylamine to produce an *acetoxime*, melting at 192°. Potassium permanganate oxidizes it to phthalic acid. It is converted into *o*-phenyl benzoic acid, on fusion with potassium hydroxide.

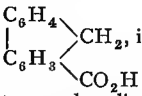
Diphenylene Glycollic Acid,  $\begin{array}{l}C_6H_4\\ |\\ C_6H_4\end{array}\!\!>C(OH).CO_2H$, is produced when phenanthraquinone is boiled with sodium hydroxide:—

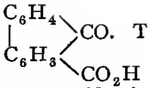


$$\begin{array}{l}C_6H_4{-}CO\\ |\qquad\quad |\\ C_6H_4{-}CO\end{array} + H_2O = \begin{array}{l}C_6H_4\\ |\\ C_6H_4\end{array}\!\!>C(OH).CO_2H;$$

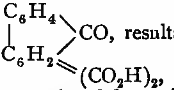
in this instance an atomic rearrangement occurs, similar to that observed in the transition of benzil to benzilic acid. It crystallizes from hot water in shining leaflets, melting at 162°. It dissolves with an indigo blue color in concentrated sulphuric acid; this color disappears on the addition of water. Carbon dioxide and water split off and *fluorene ether* results. This is also produced by heating the acid above its melting point. Chromic acid oxidizes it to diphenylene ketone. If the acid be heated to 120° with HI and P it becomes,

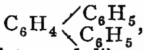
Diphenylene Acetic Acid,  $\begin{array}{l}C_6H_4\\ |\\ C_6H_4\end{array}\!\!>CH.CO_2H$,—Fluorene Carboxylic Acid. This is insoluble in water, forms indistinct crystals, and melts about 221°. Its *ethyl ester* melts at 165°. When heated above its melting point, more readily with soda-lime, it is decomposed into carbon dioxide and diphenylene methane.

α-Fluorenic Acid,  $\begin{array}{l}C_6H_4\\ |\\ C_6H_3\end{array}\!\!>CH_2,\ C_6H_3{-}CO_2H$, is formed by the action of sodium amalgam upon α-diphenylene-ketone carboxylic acid. It is almost entirely insoluble in water, and melts at 245°. It yields fluorene when distilled with lime. Potassium permanganate reproduces diphenylene-ketone carboxylic acid.

Diphenylene-ketone Carboxylic Acids, $C_{14}H_8O_3$ =  $\begin{matrix} C_6H_4 \\ | \\ C_6H_3 \end{matrix} \begin{matrix} \searrow CO. \\ \swarrow \\ \searrow CO_2H \end{matrix}$ The *a-acid* is produced by the oxidation of fluoranthene with a chromic acid mixture. It crystallizes in red needles, melting at 191°. Sodium amalgam converts it into fluorenic acid. Isodiphenic acid results when it is fused with potassium hydroxide (p. 850), while heating with lime breaks it down into carbon dioxide and diphenylene ketone; fluorene is produced if it be distilled with zinc dust.

The *β-acid* is formed upon heating silver diphenylene-ketone dicarboxylate. Yellow needles that sublime without melting. The *γ-* or *ortho-acid* is formed when diphenic acid is heated to 110° with concentrated sulphuric acid. It crystallizes from alcohol in yellow needles, melting at 223° (*Berichte*, 20, 846). Fusion with caustic potash changes it to diphenic acid. Its *oxime* melts at 263°; its *hydrazone* at 205° (*Berichte*, 22, Ref. 727).

Diphenylene-ketone Dicarboxylic Acid,  $\begin{matrix} C_6H_4 \\ | \\ C_6H_2 \end{matrix} \begin{matrix} \searrow CO, \\ \swarrow \\ \searrow (CO_2H)_2, \end{matrix}$ results when retenequinone is oxidized with potassium permanganate. A sulphur-yellow, crystalline powder, which does not melt, but above 270° breaks down into carbon dioxide and *p*-diphenylene-ketone carboxylic acid. It yields diphenyl when distilled with lime. Diphenylene-ketone is produced from the silver salt (*Berichte*, 18, 1751).

Diphenyl Benzene, $C_{16}H_{14}$ =  $C_6H_4 \begin{matrix} \nearrow C_6H_5 \\ \searrow C_6H_5 \end{matrix}$, Diphenyl Phenylene, is produced when sodium acts on a mixture of dibrombenzene, $C_6H_4Br_2$(1, 4) and C_6H_5Br, also on conducting a mixture of diphenyl and benzene through ignited tubes. Isodiphenyl benzene also results in the latter case; therefore, both are produced in the preparation of diphenyl (*Berichte*, 11, 1755).

p-Diphenyl benzene is sparingly soluble in hot alcohol and ether, easily in benzene, crystallizes in flat needles, melts at 205°, sublimes readily, and boils at 400°. Chromic acid, in glacial acetic acid, oxidizes it to *p*-diphenyl carboxylic acid (p. 849), and then to terephthalic acid. Isomeric isodiphenyl benzene melts at 85°, and boils about 360°. Chromic acid, in glacial acetic acid, oxidizes it to benzoic acid and an isomeric *m*-diphenyl carboxylic acid.

Triphenyl Benzene, $C_6H_3(C_6H_5)_3$ (1, 3, 5), is formed from acetophenone, $C_6H_5.CO.CH_3$, when heated with P_2O_5, or by conducting hydrochloric acid gas into it, when there occurs a condensation similar to that observed in the formation of mesitylene from acetone, $CH_3.CO.CH_3$ (p. 566). It crystallizes from ether in rhombic plates, melting at 169°, and distils above 360°. Chromic acid oxidizes it, in acetic acid solution, to benzoic acid (*Berichte*, 23, 2533).

2. Derivatives of benzene nuclei joined by one carbon atom.

1. DIPHENYL METHANE DERIVATIVES.

The compounds, having two benzene nuclei joined by one carbon atom, are obtained according to the following methods:—

1. Zinc dust is added to a mixture of benzyl chloride and benzene, and heat applied. An energetic reaction ensues, hydrogen

chloride escapes and diphenyl methane results (Zincke, *Annalen*, 159, 367):—

$$C_6H_5.CH_2.Cl + C_6H_6 = \underset{\text{Diphenylmethane.}}{C_6H_5.CH_2.C_6H_5} + HCl.$$

Benzyl chloride reacts similarly upon toluene, xylene and other hydrocarbons:—

$$C_5H_5.CH_2Cl + C_6H_5.CH_3 = \underset{\text{Benzyl Toluene.}}{C_6H_5.CH_2.C_6H_4.CH_3} + HCl;$$

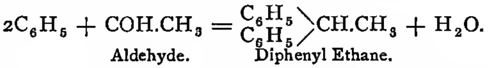
and upon phenols or their acid esters (*Berichte*, 14, 261):—

$$C_6H_5.CH_2Cl + C_6H_5.OH = C_6H_5.CH_2.C_6H_4.OH + HCl.$$

Aluminium chloride may be employed as a substitute for zinc dust (p. 569).

The tertiary anilines (compare p. 601) react similarily to the phenols on the application of heat (even without zinc); thus from benzyl chloride and dimethyl aniline we get the base, $C_6H_5.CH_2.C_6H_4N(CH_3)_2$, dimethylamido-diphenylmethane.

2. The fatty aldehydes are mixed with benzene (toluene, naphthalene, diphenyl, etc.) and concentrated sulphuric acid then added; water separates and two phenyls replace the aldehyde oxygen (Baeyer, *Berichte*, 6, 221):—



$$2C_6H_5 + \underset{\text{Aldehyde.}}{COH.CH_3} = \underset{\text{Diphenyl Ethane.}}{\begin{matrix} C_6H_5 \\ C_6H_5 \end{matrix}\!\!>\!CH.CH_3} + H_2O.$$

The acetaldehyde is applied as paraldehyde, and it is necessary to employ strongly cooled sulphuric acid. Methylene aldehyde is applied in the form of methylal, $CH_2(O.CH_3)_2$ (p. 301), or methyl diacetate:—

$$2C_6H_5 + \underset{\text{Methylal.}}{CH_2(O.CH_3)_2} = \underset{\text{Diphenylmethane.}}{(C_6H_5)_2CH_2} + 2CH_3.OH.$$

The reaction proceeds with special ease on using anhydrous chloral (or with mono-and dichlor-aldehyde) and chlorine substitution products result:—

$$2C_6H_6 + COH.CCl_3 = (C_6H_5)_2\ CH.CCl_3 + H_2O.$$

Sodium amalgam causes the replacement of the halogens in these derivatives, and we get the corresponding hydrocarbons.

The benzene hydrocarbons react with the aromatic alcohols just as they do with the aldehydes:—

$$C_6H_5.CH_2.OH + C_6H_6 = C_6H_5.CH_2.C_6H_5 + H_2O.$$

Triphenyl methane, $(C_6H_5)_2CH.C_6H_5$, is similarly formed from benzhydrol, $(C_6H_5)_2CH.OH$. Triphenyl methane derivatives are the chief products when benzaldehyde is used.

The benzenes also condense with ketones, aldehydic acids and ketonic acids. Thus from benzene and glyoxylic acid we obtain diphenylacetic acid, with pyroracemic acid, α-diphenylpropionic acid. Sometimes we get an aldol condensation with the production of oxy-compounds (p. 716); in this way dibrom-atrolactinic acid, $C_6H_5.C(OH)\left\langle\begin{matrix}CHBr_2\\CO_2H\end{matrix}\right.$, results from benzene and dibrom-pyro-racemic acid.

The aldehydes also act upon the phenols, yielding phenol-derivatives of the diphenylmethanes; here it is better to substitute $SnCl_4$ for sulphuric acid (*Berichte*, 11, 283). Thus we get diphenol ethane from paraldehyde and phenol:—

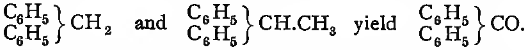
$$CH_3.CHO + 2C_6H_5.OH = CH_3.CH(C_6H_4.OH)_2 + H_2O.$$

Ethidene dinaphthyl ether, $CH_3.CH(O.C_{10}H_7)_2$ and the *condensation product*, $CH_3.CH\left\langle\begin{matrix}C_{10}H_6\\C_{10}H_6\end{matrix}\right\rangle O$ (*Berichte*, 19, 3004, 3318), are produced when acetaldehyde acts upon β-naphthol in the presence of glacial acetic acid and a little hydrochloric acid.

The tertiary anilines react like the phenols (p. 601) and *amido-derivatives* result. Instead of the aldehydes (or their ethers) we can employ their haloids, when the reaction will begin on the application of heat. For example, from methylene iodide, CH_2I_2, and dimethyl aniline we obtain the base $CH_2\left\langle\begin{matrix}C_6H_4.N(CH_3)_2\\C_6H_4.N(CH_3)_2\end{matrix}\right.$; the same product results with CCl_3H and CCl_4. Acetone and zinc chloride yield the base, $(CH_3)_2C\left\langle\begin{matrix}C_6H_4.N(CH_3)_2\\C_6H_4.N(CH_3)_2\end{matrix}\right.$ (*Berichte*, 21, Ref. 16). Such bases are also produced as by-products in the manufacture of methyl aniline and malachite green.

Benzaldehyde and the dimethyl anilines condense to amidobenzhydrols when heated with concentrated hydrochloric acid, whereas triphenylmethane derivatives result if zinc chloride, sulphuric acid and oxalic acid be used. Chloral reacts similarly with dimethylanilines, accompanied by hydrol condensation (*Berichte*, 21, 3299).

If the hydrocarbons be oxidized with a chromic acid mixture they yield *ketones*, and the group CH_2 or CHR is converted into CO. From dimethyl methane and dimethyl ethane we obtain diphenyl ketone:—



$$\left.\begin{matrix}C_6H_5\\C_6H_5\end{matrix}\right\}CH_2 \quad \text{and} \quad \left.\begin{matrix}C_6H_5\\C_6H_5\end{matrix}\right\}CH.CH_3 \quad \text{yield} \quad \left.\begin{matrix}C_6H_5\\C_6H_5\end{matrix}\right\}CO.$$

Should alkyls be present in the benzene nucleus these are oxidized to carboxyls:—

$$\underset{\text{Benzyl Toluene.}}{C_6H_5.CH_2.C_6H_4.CH_3} \quad \text{yields} \quad \underset{\text{Benzoyl Benzoic Acid.}}{C_6H_5.CO.C_6H_4.CO_2H.}$$

Such ketones are further produced:—

1. If benzoic acid or its anhydride be heated with benzenes and P_2O_5 (*Merz*). A condensation similar to that of the hydrocarbons takes place here:—

$$\underset{\text{Benzoic Acid.}}{C_6H_5.CO.OH} + C_6H_6 = \underset{\text{Diphenyl Ketone.}}{C_6H_5.CO.C_6H_5} + H_2O.$$

2. By the action of benzoyl chloride on benzenes, in the presence of aluminium chloride (comp. p. 853):—

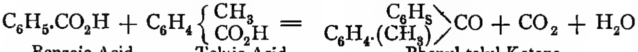
$$\underset{\text{Benzoyl Chloride.}}{C_6H_5.COCl} + \underset{\text{Toluene.}}{C_6H_5.CH_3} = \underset{\text{Phenyl tolyl Ketone.}}{C_6H_5.CO.C_6H_4.CH_3} + HCl.$$

Phosgene reacts in the same manner, and acid chlorides are the first products (comp. p. 739):—

$$COCl_2 + 2C_6H_6 = C_6H_5.CO.C_6H_5 + 2HCl.$$

3. According to the general method of producing ketones, on heating the calcium salts with aromatic acids:—

$$\underset{\text{Benzoic Acid.}}{C_6H_5\,CO_2H} + \underset{\text{Benzoic Acid.}}{C_6H_5.CO_2H} = \underset{\text{Diphenyl Ketone.}}{(C_6H_5)_2CO} + CO_2 + H_2O,$$



$$\underset{\text{Benzoic Acid.}}{C_6H_5.CO_2H} + \underset{\text{Toluic Acid.}}{C_6H_4\left\{\begin{matrix}CH_3\\CO_2H\end{matrix}\right.} = \underset{\text{Phenyl-tolyl Ketone.}}{\left.\begin{matrix}C_6H_5\\C_6H_4.(CH_3)\end{matrix}\right\rangle CO} + CO_2 + H_2O$$

On heating with zinc dust or hydriodic acid and amorphous phosphorus, the ketones sustain a reduction of the CO group and revert to the hydrocarbons, for example, diphenyl ketone yields diphenyl methane. Sodium amalgam changes them to secondary alcohols:—

$$(C_6H_5)_2CO + H_2 = (C_6H_5)_2CH.OH.$$

Pinacones are simultaneously produced through the union of two molecules (see benzpinacone).

The *oxy-ketones* and *ketone phenols* are produced from the phenols by the action of benzoyl chloride, by heating with zinc chloride, or more readily with aluminium chloride; further by heating benzo-trichloride, $C_6H_5.CCl_3$, with phenols and zinc oxide:—

$$C_6H_5.COCl + C_6H_5.OH = \underset{\text{Benzoyl Phenol.}}{C_6H_5.CO.C_6H_4.OH} + HCl,$$

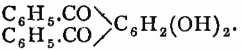
$$C_6H_5.CCl_3 + C_6H_5.OH + ZnO = C_6H_5.CO.C_6H_4.OH + ZnCl_2 + HCl.$$

The reaction is analogous to the action of chloroform upon phenols in alkaline solution, when aldehyde phenols (oxy-aldehydes) are obtained (p. 723).

Instead of the free phenols it is better to use the benzoyl esters of the phenols (*e. g.*, $C_6H_5.O.C_7H_5O$). The first products are the benzoyl esters of the phenol ketones, *e. g.*, $C_6H_5.CO.C_6H_4.O.C_7H_5O$, which yield the free phenol ketones when saponified with alcoholic potassium hydroxide (*Berichte*, 10, 1969). In the use of the free phenols we get, on the contrary (especially with $C_6H_5.CCl_3$, even by gentle digestion), dye substances, which belong to the aurine series, and are derived from triphenyl methane.

When benzoyl chloride and zinc chloride act on the divalent phenols (their benzoyl esters) *e. g.*, resorcin, we obtain their mono- and di-ketones (*Berichte*, 12, 661), as—

$C_6H_5.CO.C_6H_3(OH)_2$ and



$$\left.\begin{matrix}C_6H_5.CO\\C_6H_5.CO\end{matrix}\right\rangle C_6H_2(OH)_2.$$

Zinc chloride converts salicylic acid, $C_6H_4(OH).CO_2H$, and phenol into salicylphenol, $C_6H_4(OH).CO.C_6H_4.OH$ (*Berichte*, 14, 656).

We can also derive the *amido-ketones*, *e. g.*, $C_6H_5.CO.C_6H_4.NH_2$, by methods similar to those employed with the ketones and oxy-ketones:—

1. By heating benzoic acid with tertiary anilines and P_2O_5:—

$$C_6H_5.CO.OH + C_5H_5.N(CH_3)_2 = C_6H_6.CO.C_6H_4.N(CH_3)_2 + H_2O,$$

whereas, by the action of benzoyl chloride two benzoyl groups enter the benzene nucleus (*Annalen*, 206, 88); 2. By the action of benzoyl chloride upon primary anilines, in which both amide hydrogens are replaced by acid radicals (as in phthalanile, $C_6H_6.N(CO)_2C_6H_4$ (p. 611), on heating alone, or with zinc chloride or aluminium chloride:—

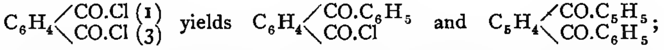
$$C_6H_5.COCl + C_6H_5.N(CO.R)_2 = C_6H_5.CO.C_6H_4.N(CO.R)_2 + HCl.$$

The free amido-ketones are obtained by the saponification of these anilides (*Berichte*, 14, 1836).

Furthermore, *ketonic acids* and diketones are produced according to these methods. For example, we obtain meta-benzoyl benzoic acid (its chloride) from benzoyl chloride and benzoic anhydride, witb zinc chloride (*Berichte*, 14, 647):—

$$2C_5H_6.COCl + (C_6H_5.CO)_2O = \underset{\text{Benzoyl Benzoic Acid.}}{2C_6H_5.CO.C_6H_4.COCl} + H_2O,$$

and meta benzoyl benzoic acid together with so-called isophthalphenone (*Berichte*, 13, 321; 19, 146) from isophthalic chloride and benzene by means of $AlCl_3$:—



$$C_6H_4\begin{cases}CO.Cl\ (1)\\CO.Cl\ (3)\end{cases} \text{ yields } C_6H_4\begin{cases}CO.C_6H_5\\CO.Cl\end{cases} \text{ and } C_5H_4\begin{cases}CO.C_5H_5\\CO.C_6H_5\end{cases};$$

o-benzoylbenzoic acid is obtained from phthalic anhydride and benzene with aluminum chloride. It is further converted into *o*-diphenyl phthalide (p. 880). The latter can be directly obtained from *o*-phthalyl chloride and benzene by means of $AlCl_3$.

Diphenyl Methane, $C_{13}H_{12} = C_6H_5.CH_2.C_6H_5$, Benzyl benzene, is obtained according to the synthetic methods already mentioned: from benzyl chloride and benzene with zinc dust or $AlCl_3$; from formic aldehyde or benzyl alcohol and benzene with sulphuric acid; and from CH_2Cl_2 (or $CHCl_3$) with benzene and $AlCl_3$ (together with anthracene).

In the preparation of diphenyl methane, 10 parts of benzyl chloride are digested with 6 parts of benzene and zinc dust, etc.; the latter only induces the reaction and when this has commenced it can be filtered off (*Annalen*, 159, 374). A better method is that of Friedel. It consists in digesting 10 parts benzyl chloride with 50 parts benzene and 3–4 parts of $AlCl_3$.

Diphenyl methane is easily soluble in alcohol and ether, possesses the odor of oranges, crystallizes in needles, melts at 26.5°, and boils at 262°. When conducted through ignited tubes it yields diphenylene methane (p. 850); a chromic acid mixture oxidizes it to diphenyl ketone.

When treated with bromine in the heat it yields $(C_6H_5)_2CHBr$, diphenyl-brom-methane, and $(C_6H_5)_2CBr_2$ diphenyl dibrom-methane; the former melts at 45°, and the latter is a brown crystalline mass.

Nitrodiphenyl Methane, $C_6H_5.CH_2.C_6H_4.NO_2$. The *ortho*-compound is prepared from *o*-nitrobenzyl chloride and benzene with $AlCl_3$. It is liquid and when oxidized by chromic acid and acetic acid yields *o*-nitro-benzophenone. The *meta*- and *para*-bodies are derived from meta- and para-nitro-benzyl alcohol (p. 709) by means of benzene and sulphuric acid. The first is an oil; the second melts at 31° (*Berichte*, 18, 2402).

Diphenyl methane dissolves in concentrated nitric acid yielding *two dinitro-derivatives*, the α- melting at 183°, and the β-variety at 118° (*Berichte*, 21, 1347; 23, 2578). Further nitration with nitric-sulphuric acid produces **Tetranitro-diphenyl Methane,** $[C_6H_3(NO_2)_2]_2CH_2$; yellow prisms, melting at 172°. It forms dark blue colored salts with alcoholic potash (p. 861 and *Berichte*, 22, 2445).

Diphenyldinitro Methane, $(C_6H_5)_2C(NO_2)_2$, results from the action of N_2O_4 upon benzophenoxime (similar to the formation of pseudo-nitriles, p. 109). Colorless leaflets, melting at 78° (*Berichte*, 23, 3491).

The reduction of the α-dinitro-product yields **α-Diamido-diphenyl methane,** $(C_6H_4.NH_2)_2CH_2$ (dipara); shining leaflets, melting at 85°. Its *tetramethyl derivative*, $[C_6H_4.N(CH_3)_2]_2CH_2$, results from dimethyl aniline by means of $C_2H_2I_2(CCl_3H$ and $CCl_4)$, or with methylal (p. 853), and as a by-product in the manufacture of malachite green. It crystallizes in shining leaves, melts at 90°, and distils undecomposed. It yields a blue dyestuff by oxidation.

The hydrogen of the group CH_2, attached to *basic* radicals *is very readily replaced by sulphur;* so that by heating with sulphur to 230° we obtain the *thio*-compound, $CS[C_6H_4.N(CH_3)_2]_2$. Benzylaniline, $C_6H_5.CH_2.NH.C_6H_5$ (*Annalen*, 259, 300) reacts similarly.

β-Diamido-diphenyl Methane, $(C_6H_4.NH_2)_2CH_2$, from the β-dinitro-compound, melts at 88°.

Oxy-diphenyl Methane, $C_6H_5.CH_2.C_6H_4.OH$ (para-), *Benzyl phenol*, obtained from benzyl chloride and phenol, melts at 84° and boils at 320°.

Dioxydiphenyl Methane, $CH_2(C_6H_4.OH)_2$ (dipara), is produced on fusing diphenyl methane disulphonic acid with KOH. It crystallizes in shining leaflets or needles, melts at 158° and sublimes. By stronger heating with caustic potash (300°), it decomposes into para-oxybenzoic acid and phenol. Its *dimethyl ether*, $CH_2(C_6H_4.O.CH_3)_2$, is formed from anisol and methylal, and melts at 52°.

Diphenyl Carbinol, $(C_6H_5)_2CH.OH$, *Benzhydrol*, is produced on heating diphenyl brom-methane, $(C_6H_5)_2CHBr$, with water to 150°, more readily from diphenyl ketone $(C_6H_5)_2CO$, with sodium amalgam, or by heating with alcoholic potassium hydroxide and zinc dust (together with benzpinacone). It is sparingly soluble in water, easily in alcohol and ether, crystallizes in silky needles, melts at 68°, and boils at 298° under partial decomposition into water, and *benzhydrol ether*, $[(C_6H_5)_2.CH]_2O$, melting at 109°.

The benzhydrol *amide derivatives* may be synthesized by the condensation of benzaldehyde with dimethyl-anilines upon heating them with hydrochloric acid (sulphuric acid, zinc chloride and oxalic acid produce triphenyl derivatives, *Berichte*, 21, 3293):—

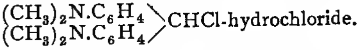
$$C_6H_5.CHO + C_6H_5.NR_2 = \underset{\text{Dimethyl-amido-benzhydrol.}}{C_6H_5.CH(OH).C_6H_4.NR_2.}$$

Mono-amido-derivatives, such as these, dissolve in acids, forming colorless or slightly colored compounds.

p-Nitrodimethyl-amidobenzhydrol, $NO_2.C_6H_4.CH(OH).C_6H_4.N(CH_3)_2$, results in the condensation of *p*-nitrobenzaldehyde with dimethyl aniline on heating them with hydrochloric acid. Yellow needles, melting at 96°. Zinc dust and hydrochloric acid reduce it to

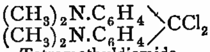
Unsymmetrical **Dimethyldiamidobenzhydrol**, $H_2N.C_6H_4.CH(OH).C_6H_4.N(CH_3)_2$, melting at 165°.

Tetramethyl-diamidobenzhydrol, $\left\{\begin{matrix}(CH_3)_2N.C_6H_4\\(CH_3)_2N.C_6H_4\end{matrix}\right>CH.OH$, has been prepared by reducing tetramethyldiamidobenzophenone (p. 859). Such diamidodiphenylhydrol bases are colorless, but when *digested with acids yield deep blue colored salts*, corresponding to the rosaniline salts (*Berichte*, 21, 3298); they very probably are benzhydrol or carbinol salts :—



$$\left\{\begin{matrix}(CH_3)_2N.C_6H_4\\(CH_3)_2N.C_6H_4\end{matrix}\right>CHCl\text{-hydrochloride.}$$

Perfectly analogous compounds are :—



$$\left\{\begin{matrix}(CH_3)_2N.C_6H_4\\(CH_3)_2N.C_6H_4\end{matrix}\right>CCl_2$$

Tetramethyldiamido-
benzophenone Chloride.

and

$$\left\{\begin{matrix}(CH_3)_2N.C_6H_4\\(CH_3)_2N.C_6H_4\end{matrix}\right>CS;$$

Tetramethyldiamido-
thiobenzophenone.

they are derivatives of diamidobenzophenone, and have a salt-like character. The first is dark-blue in color, while the second is a crystalline powder, showing a cantharides-green color. Its solutions are green or dark red in color (*Berichte*, 20, 1732).

Benzophenone, Diphenyl Ketone, $(C_6H_5)_2CO$, is obtained according to the general methods and by heating mercury phenyl, $(C_6H_5)_2Hg$, with benzoyl chloride. It is prepared (along with benzene) on distilling calcium benzoate, or from benzoyl chloride and benzene with $AlCl_3$; most easily by adding $AlCl_3$ to the solution of $COCl_2$ in benzene (*Berichte*, 10, 1854). It is dimorphous; generally crystallizes in large rhombic prisms, melting at 48–49°, sometimes in rhombohedra, which melt at 27° and gradually change to the first modification. It has an aromatic odor, and boils at 295°. When fused with alkalies it decomposes into benzoic acid and benzene; if it be heated with zinc dust diphenyl methane is produced.

PCl_5 converts it into the chloride $(C_6H_5)_2CCl_2$. A liquid, boiling at 220°. Hot water changes it to benzophenone. Hydroxylamine converts benzophenone into

Benzophenoxime, $(C_6H_5)_2C:N.OH$, crystallizing in needles, melting at 140° (*Berichte*, 19, 989). An isomeric benzophenoxime could not be obtained, while unsymmetrical benzophenones, *e. g.*, brombenzophenone and phenylethyl ketone, each form two oximes (pp. 727, 718).

Benzophenoxime (like other ketone oximes, p. 727), when digested at 100° with sulphuric acid, with hydrochloric acid and acetic acid, etc., sustains the following peculiar molecular rearrangement (*Berichte*, 22, Ref. 591) :—

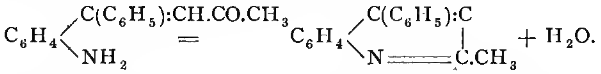
$$C_6H_5.C(N.OH).C_6H_5 = C_6H_5.CO.NH.C_6H_5, \text{ Benzanilide.}$$

The isomeric benzanilide imide-chloride is produced in like manner from the imide chloride formed by PCl_5 (p. 744). Phenylhydrazine and benzophenone unite when their alcoholic solution is warmed, forming the *phenylhydrazone*, $(C_6H_5)_2C:N_2H.C_6H_5$, crystallizing in delicate needles, melting at 137° (*Berichte*, 19, Ref. 302).

Nitrobenzophenones, $C_6H_5.CO.C_6H_4(NO_2)$. The three isomerides are produced by the oxidation of the three nitrodiphenyl-methanes (p. 857). The *meta* compound has also been obtained from *m*-nitrobenzoyl chloride with benzene and $AlCl_3$. It melts at 94° (*Berichte*, 18, 2401).

Dinitrobenzophenones, $C_6H_4(NO_2).CO.C_6H_4(NO_2)$. The α-body is produced by oxidizing α-dinitro-diphenylmethane. It melts at 190°. The β- and γ-bodies are formed by the nitration of benzophenone with fuming nitric acid. The former melts at 190°; the latter at 149°.

Amidobenzophenones, $C_6H_5.CO.C_6H_4(NH_2)$, *Benzoanilines*. The three isomerides are produced by the reduction of the three nitrobenzophenones with tin and hydrochloric acid. The *ortho* melts at 106°, and condenses with acetone, by the action of caustic soda (same as *o*-amido benzaldehyde, p. 720), forming γ-phenyl-α-methylquinoline (*Berichte*, 18, 2405):—



$$C_6H_4\left\langle\begin{matrix}C(C_6H_5):CH.CO.CH_3\\NH_2\end{matrix}\right. = C_6H_4\left\langle\begin{matrix}C(C_6H_5):C\\ \qquad\qquad\ |\\N=\!=\!=\!=C.CH_3\end{matrix}\right. + H_2O.$$

Meta-amidobenzophenone melts at 87°. The *para* compound is produced when benzanilide or phthalanile is heated with benzoyl chloride and zinc chloride; the anilides formed at first being saponified (p. 858). Colorless needles or leaflets, melting at 124° (*Berichte*, 18, 2404).

Upon methylating *p* amidobenzophenone we obtain **Dimethyl *p* amidobenzophenone**, $C_6H_5.CO.C_6H_4.N(CH_3)_2$. It can also be prepared by the decomposition of malachite green with hydrochloric acid (*Berichte*, 21, 3293).

Diamidobenzophenones are formed by reducing dinitrobenzophenones, and by the decomposition of the rosanilines.

α-**Diamidobenzophenone**, $CO(C_6H_4.NH_2)_2$, is produced from α-dinitrobenzophenone and by the breaking down of pararosaniline. It consists of large plates, melting at 237° and forms substantive tetrazo dyestuffs (*Berichte*, 22, 988).

Tetramethyl-diamidobenzophenone, $CO\left\langle\begin{matrix}C_6H_4.N(CH_3)_2\\C_6H_4.N(CH_3)_2\end{matrix}\right.$, results upon heating hexamethyl violet with hydrochloric acid (*Berichte*, 19, 109). It is technically prepared by the action of $COCl_2$ upon dimethyl aniline in the presence of $AlCl_3$, and serves for the production of hexamethyl violet. From alcohol it crystallizes in yellow leaflets, melting at 173° (*Berichte*, 22, 1876). Being a ketone it unites with hydroxylamine and phenylhydrazine (*Berichte*, 20, 1111). Dimethylaniline (and PCl_3) converts it into methyl violet, while it yields *Victoria blue* (p. 876) with phenylnaphthylamine, $C_{10}H_7.NH.C_6H_5$.

When heated with ammonium chloride and zinc chloride a base is produced, the salts of which have a beautiful yellow color. The hydrochloride, $\left.\begin{matrix}(CH_3)_2.N.C_6H_4\\(CH_3)_2N.C_6H_4\end{matrix}\right\rangle C:NH.HCl$, crystallizing in golden yellow leaflets, is **auramine**, important as a cotton dye. Cotton mordanted with tannin is colored a beautiful yellow by this salt. Perfectly analogous dyestuffs are obtained from the primary anilines and diamines (*Berichte*, 20, 2844).

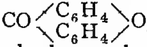
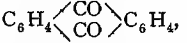
Thiobenzophenone, $(C_6H_5)_2CS$, is derived from benzene by means of $CSCl_2$ and $AlCl_3$. It is a reddish-brown oil. Hydroxylamine converts it into benzophenoxime, and with hydroxylamine it yields a hydrazone (*Berichte*, 21, 341).

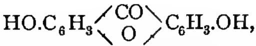
The *Thiobenzophenone* (melting at 146°), derived from benzophenone chlorimide and potassium sulphide, appears to be a polymeride.

Tetramethyldiamido-thiobenzophenone, $CS[C_6H_4.N(CH_3)_2]_2$, results from the action of hydrogen sulphide or carbon disulphide upon the auramines; the imide group is displaced. It is technically prepared from dimethylaniline and $CSCl_2$ (*Berichte*, 20, 1731 and 2857). It consists of ruby-red crystalline leaflets or a cantharides-green crystalline powder, melting at 162° (202°). In transmitted light its benzene and carbon disulphide solutions show a red color, while they are green in reflected light. When boiled with hydrochloric acid hydrogen sulphide splits off and tetramethyldiamido-benzophenone results.

Oxybenzophenones, $C_6H_5.CO.C_6H_4(OH)$, Benzoyl Phenols. The *para* is obtained from *p*-amidobenzophenone with nitrous acid (*Berichte*, 18, 2404) and from phenol with benzoyl chloride or $C_6H_5.CCl_3$ (p. 854). It is soluble in hot water. It melts at 134°, and when fused with caustic potash decomposes into benzene and para-oxybenzoic acid.

Dioxybenzophenones, $CO(C_6H_4.OH)_2$. The *dipara* is obtained from dioxydiphenyl methane by oxidizing the dibenzoyl ester with chromic acid in glacial acetic acid and saponifying with alkalies; also by the decomposition of aurine, benzaurine, phenolphtaleïn, and rosaniline (*Berichte*, 16, 1931) on heating with water or caustic alkali. It crystallizes from hot water in needles or leaflets, melts at 210°, and decomposes on fusion with caustic potash into para oxy-benzoic acid and phenol. It yields an *acetoxime* with hydroxylamine.

The *diortho*-compound is formed by fusing diphenylene ketone with caustic potash (*Berichte*, 19, 2609). It separates in the form of an oil, that solidifies with difficulty. It boils about 330-340°. It combines with hydroxylamine and phenylhydrazine. Stronger fusion with caustic potash resolves it into phenol and salicylic acid. The anhydride of diortho-dioxybenzophenone is **Diphenylene Ketone Oxide,**  $CO\left\langle\begin{matrix}C_6H_4\\C_6H_4\end{matrix}\right\rangle O$, or  $C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle C_6H_4$, *Xanthone*, produced from salicylic phenyl ether or phenylsalicylic acid by the action of concentrated sulphuric acid (*Berichte*, 21, 502). It is volatile with steam, crystallizes in yellow needles, melting at 174°, and boiling at 250°. It is rather singular that it does not unite with hydroxylamine or phenylhydrazine. When reduced with HI it affords *methylene diphenyl oxide*, $CH_2(C_6H_4)_2O$. White leaflets, melting at 99° and boiling at 312°. It forms dioxy-benzophenone on fusion with KOH.

Dioxydiphenylene-Ketone Oxide, $C_{13}H_8O_4 =$  $HO.C_6H_3\left\langle\begin{matrix}CO\\O\end{matrix}\right\rangle C_6H_3.OH$, *Euxanthone*, occurs together with euxanthinic acid in Indian yellow (jaune indien). The latter is resolved into glycuronic acid (p. 491) and euxanthone when heated with dilute sulphuric acid. It has been synthetically produced by the action of acetic anhydride upon *β*-resorcylic acid and hydroquinone carboxylic acid (*Berichte*, 23, 13; *Annalen*, 254, 265). It crystallizes in yellow needles or leaves, melting at 237°, and then subliming. It is reduced to methylenediphenylene oxide by distillation with zinc dust.

Trioxybenzophenone, $C_6H_2(OH)_3.CO.C_6H_5$, is formed by fusing pyrogallol and benzoic acid with zinc chloride at 145°. It crystallizes in yellow needles with one molecule of water, and melts at 138°. It forms *orange yellow dyestuffs* with mordants. Many other polyoxybenzophenones have been obtained by analogous methods (*Berichte*, 23, Ref. 43).

Diphenyl Ethane, $C_{14}H_{14} = (C_6H_5)_2CH.CH_3$ (isomeric with dibenzyl), is obtained from benzene and paraldehyde with sulphuric acid, from β-bromethyl benzene, $C_6H_5.CHBr.CH_3$, and benzene with zinc dust, from benzene and $CH_3.CHCl_2$ with $AlCl_3$. It is a liquid, boiling at 268–271°, and in the cold becomes a crystalline solid. Chromic acid oxidizes it to benzophenone. Nitric acid does not oxidize its side chains (*Berichte*, 17, Ref. 674). **Diphenyl trichlorethane,** $(C_6H_5)_2CH.CCl_3$, formed from benzene and chloral, consists of leaflets, melting at 64°. Alkalies convert it into diphenyldichlor-ethylene, melting at 80° and boiling at 316° (*Berichte*, 22, 760). *Diphenyltribromethane* melts at 89°. Sodium amalgam reduces both to diphenyl ethane.

Mono-chlor-aldehyde (mono-chlor-acetal or dichlorether) and benzene yield **Diphenyl mono-chlor-ethane,** $(C_6H_5)_2CH.CH_2Cl$, a thick oil, which on boiling is converted into

Diphenyl Ethylene, $C_{14}H_{12} = (C_6H_5)_2C{:}CH_2$. This is isomeric with stilbene, is also formed from *a* dibrom-ethylene, $CH_2{:}CBr_2$, by means of benzene and $AlCl_3$, and is an oil, boiling at 277°. Chromic acid oxidizes it to diphenyl ketone.

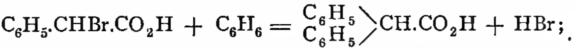
Perfectly analogous, unsaturated hydrocarbons are also obtained from toluene, xylene, naphthalene, etc. If diphenyl monochlorethane (or its analogues) be heated alone hydrochloric acid is withdrawn, and there results, not diphenyl ethylene, but, by molecular transposition, isomeric stilbene (and its analogues) :—

$$(C_6H_5)_2CH.CH_2Cl = \underset{\text{Stilbene.}}{C_6H_5.CH{:}CH.C_6H_5} + HCl.$$

Diphenylacetaldehyde, $(C_6H_5)_2.CH.CHO$, is produced by the action of sulphuric acid upon hydrobenzoin (*Berichte*, 22, Ref. 10).

Diphenylaceto-nitrile, $(C_6H_5)_2CH.CN$, results when diphenylbrommethane is heated with $Hg(CN)_2$ to 165°, or is obtained from diphenylacetic acid through the amide (*Berichte*, 22, Ref. 198). Crystallized from ether it forms brilliant prisms, melting at 72° and boiling about 184° (at 12 mm). The hydrogen of its CH-group is readily replaced by alkyls. Iodine, acting upon its sodium derivatives, produces tetraphenyl-succino-nitrile, $(C_6H_5)_4C_2(CN)_2$ (*Berichte*, 22, 1227).

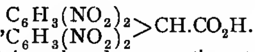
Diphenyl Acetic Acid, $C_{14}H_{12}O_2 = (C_6H_5)_2CH.CO_2H$, is formed: by the action of zinc dust on a mixture of phenyl-bromacetic acid (p. 754) and benzene :



$$C_6H_5.CHBr.CO_2H + C_6H_6 = \begin{matrix}C_6H_5\\C_6H_5\end{matrix}\!\!>CH.CO_2H + HBr;$$

from diphenyl brom-methane, $(C_6H_5)_2CHBr$, by means of the cyanide; and by heating benzilic acid to 150° with hydriodic acid. The acid crystallizes from water in needles, from alcohol in leaflets, melting at 146°. When oxidized with a chromic acid mixture it yields benzophenone; and when heated with soda lime we get diphenyl methane. Its *ethyl ester* melts at 58°; the *methyl ester* at 60° (*Berichte*, 21, 1318).

Bi-dinitro-diphenyl Acetic Acid,



$\begin{matrix}C_6H_3(NO_2)_2\\C_6H_3(NO_2)_2\end{matrix}\!\!>CH.CO_2H.$

The *ethyl ester* is derived from dinitro-phenyl acetoacetic ester and dinitro-phenyl-malonic ester (pp. 764, 791) by the action of *op*-dinitrobrombenzene; the group, $CO.CH_3$ (and $CO_2.C_2H_5$) being replaced. It may be similarly prepared from dinitro-phenyl-acetic ester (p. 754) (*Berichte*, 21, 2470). It dissolves with difficulty in alcohol and ether, and crystallizes from alcohol in colorless prisms, melting at 154°. Alcoholic potash or soda converts the ester, by the substitution of the hydrogen of the CH-group, into brilliant metallic salts, dissolving in alcohol and water, with *a dark blue color.* All methane derivatives react in like manner, provided they contain *two or three nitrophenylene groups*, *e. g.*, bi-dinitro-phenyl-methane, $[C_6H_8NO_2)_2]_2CH_2$ (p. 857) and ternitrophenyl methane $(C_6H_4NO_2)_3CH$ (p. 866) (*Berichte*, 22, 2476).

Diphenyl Glycollic Acid, Benzilic Acid, $(C_6H_6)_2C(OH).CO_2H$, is produced by a molecular rearrangement of benzil (see this) when digested with alcoholic potassium hydroxide, and from diphenyl acetic acid by the action of bromine vapor and boiling with water. We can prepare it by fusing benzil with caustic potash (*Berichte*, 14, 326); or better by the action of aqueous potash and air upon benzoïn (*Berichte*, 19, 1868). Anisilic, cuminilic and dibenzyl glycollic (see benzoïn group) acids are perfect analogues of benzilic acid.

Benzilic acid is very readily soluble in hot water and alcohol, crystallizes in needles and prisms, melts at 159°, and is of a deep red color. It dissolves with a dark red color in sulphuric acid. It yields diphenyl acetic acid when heated with hydriodic acid: on distilling its barium salt it breaks up into carbon dioxide and benzyhydrol; oxidation yields benzophenone. For the derivatives of benzilic acid, see *Berichte*, 22, 1213, 1537.

Benzyl Toluenes, Phenyl tolyl methanes, $C_{14}H_{14} = C_6H_5.CH_2.C_6H_4.CH_3$. A liquid mixture of ortho- and para-benzyl toluene, which cannot be separated, is obtained by the action of zinc dust on a mixture of benzyl chloride and toluene; by heating benzyl chloride to 190° with water, or toluene to 250° with iodine. The pure *para*-body has been formed by heating para-phenyl tolyl ketone with zinc dust, and is a liquid, boiling at 285°.

When it is oxidized with a chromic acid mixture we get the corresponding phenyl tolyl ketones and benzoyl benzoic acids.

Phenyl-tolyl Ketones, $C_{14}H_{12}O = C_6H_5.CO.C_6H_4.CH_3$. A mixture of the ortho- and para-compounds is obtained when benzoyl chloride and toluene are heated with zinc dust (in small quantity), by the distillation of a mixture of calcium benzoate and para-toluate, or by heating benzoic acid and toluene with P_2O_5. The product is an oil, from which the para-body may be crystallized out by cooling, while the ortho-derivative remains liquid.

The *para* compound is dimorphous, crystallizing in hexagonal prisms, melting at 55°, and in monoclinic prisms, melting at 58–59°. The latter modification is the more stable. It boils at 310-312°, and is sparingly soluble in alcohol. When heated with soda lime it decomposes into benzene and paratoluic acid; chromic acid converts it into parabenzoyl benzoic acid. Sodium amalgam transforms paraketone into **phenyl paratolyl carbinol**, $\begin{matrix}C_6H_5\\C_7H_7\end{matrix}\!\!>\!CH.OH$, consisting of shining needles, melting at 52°.

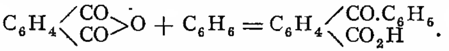
Phenyl-ortho-tolyl Ketone is a liquid and boils about 316°.

A characteristic feature is the ability of the ortho-, but not the para-derivatives, to change readily to anthracene and its derivatives, in consequence of an ortho-condensation of the two benzene nuclei (p. 850). Thus anthracene is produced on conducting phenyl-tolyl methane through an ignited tube or upon heating the ketone with zinc dust, and we obtain anthraquinone (see anthracene) on heating ortho-phenyl-tolyl-ketone with lead oxide.

Other diphenyl ketones, containing a methyl group in the ortho position, relatively to the ketone group, are prepared in a similar manner, see *Berichte*, 18, 1797.

Benzoyl Benzoic Acids, $C_{14}H_{10}O_4 = C_6H_5.CO.C_6H_4.CO_2H$, result from the oxidation of the phenyl tolyl methanes or phenyl-tolyl ketones, and can be synthesized by the methods given upon p. 856.

The *para*-acid crystallizes and sublimes in leaflets, melting at 194°. The *meta*-acid, from isophthalic chloride and benzene, consists of needles, melting at 161°. The *ortho*-acid is most readily obtained from phthalic anhydride, benzene and $AlCl_3$ (p. 856):—

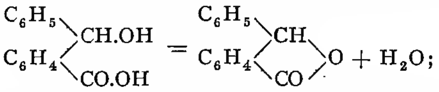


$$C_6H_4\left<\begin{matrix}CO\\CO\end{matrix}\right>O + C_6H_6 = C_6H_4\left<\begin{matrix}CO.C_6H_5\\CO_2H\end{matrix}\right..$$

It crystallizes with 1 molecule of H_2O, which is lost at 110°, and it then melts at 127°. Heated to 180° with phosphorus pentoxide, water is eliminated, and anthraquinone is produced; in the same manner we get anthraquinone sulphonic acid by digestion with fuming sulphuric acid. Anthracene is produced when it is heated with zinc dust. With benzene and aluminium chloride orthobenzoyl-benzoic acid yields phthalophenone, with phenol and stannic chloride oxyphthalophenone (see phthaleïns).

If tin and hydrochloric acid or sodium amalgam be allowed to act on the alcoholic solution of the para-acid we obtain **Para-benzhydryl-benzoic Acid,** $C_6H_5.CH(OH).C_6H_4.CO_2H$, melting at 165°, and passing back into benzoyl benzoic acid when oxidized. Heated to 160° with hydriodic acid, it yields **benzyl benzoic acid,** $C_6H_5.CH_2.C_6H_4.CO_2H$, which is also produced in small quantity from benzyl toluene by oxidation with nitric acid. This melts at 157°, and is rather readily soluble in hot water. Chromic acid oxidizes it to benzoyl benzoic acid. Diphenyl methane is produced on heating it with soda-lime.

In the same manner ortho-benzoyl benzoic acid forms **ortho-benzhydryl-benzoic acid,** $C_6H_5.CH(OH).C_6H_4.CO_2H$, by reduction. This acid, however, does not exist in a free condition, but at the moment of its liberation from its salts decomposes, like all the γ-oxyacids, into water and its lactone, *Phenyl phthalide*:—



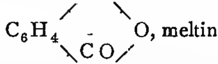
$$\begin{matrix}C_6H_5\\C_6H_4\end{matrix}\!\!>\!CH.OH\ \ \ ... $$

$$\left.\begin{matrix}C_6H_5\diagdown\\ \\ C_6H_4\diagup\end{matrix}\right.\begin{matrix}CH.OH\\ \\ \diagdown CO.OH\end{matrix} = \left.\begin{matrix}C_6H_5\diagdown\\ \\ C_6H_4\diagup\end{matrix}\right.\begin{matrix}CH\diagdown\\ \\ \diagdown CO\diagup\end{matrix}O + H_2O;$$

this is similar to the formation of phthalide (p. 772), from *o*-oxymethyl benzoic acid. The lactone, $C_{14}H_{10}O_2$, is insoluble in water, crystallizes from hot alcohol and ether in needles, and melts at 115°. It is only after protracted warming with alkalies that it can be transformed into salts of orthobenzhydryl-benzoic acid. Like orthophenyl-tolyl ketone and ortho-benzyl benzoic acid, it is easily changed into anthraquinone.

Ditolyl Methane, $CH_2\left<\begin{matrix}C_6H_4.CH_3\\C_6H_4.CH_3\end{matrix}\right.$, **Ditolyl Ketone,** $CO\left<\begin{matrix}C_6H_4.CH_3\\C_6H_4.CH_3\end{matrix}\right.$, **Ditolyl Ethane,** $CH_3.CH(C_6H_4.CH_3)_2$, etc. (*Berichte,* 18, 665), are produced like the phenyl compounds and yield derivatives that correspond very closely to them. Ditolyl chlor-ethane, $CH_2Cl.CH(C_6H_4.CH_3)_2$, yields on the one hand (by alcoholic potash) ditolyl ethylene, $CH_2:C(C_6H_4.CH_3)_2$, upon the other, by aid of heat (through molecular rearrangement), dimethyl stilbene, $CH_3.C_6H_4CH:CH.C_6H_4.CH_3$ (comp. p. 861).

Tolu-benzoic Acids, $CO{<}\begin{smallmatrix}C_6H_4.CH_3\\C_6H_4.CH_3\end{smallmatrix}$. The *para*-acid is produced by oxidizing ditolyl methane and ditolyl ethane (together with ditolyl ketone). It melts at 228°. *p*-Tolu-*o*-benzoic acid results (analogous to *o*-benzoyl benzoic acid) from phthalic anhydride, toluene and $AlCl_3$. It contains one molecule of water of crystallization and when anhydrous melts at 146°. It forms *β*-methyl anthracene when heated with zinc dust. Zinc and hydrochloric acid reduce it to an oxyacid, which changes, on liberation, into its lactone,



$C_6H_4{<}\begin{smallmatrix}CH.C_6H_4.CH_3\\CO\end{smallmatrix}{>}O$

Tolylphthalide, C_6H_4 O, melting at 129°. Xylene and mesitylene yield similar derivatives with phthalic anhydride (*Berichte*, 19, Ref. 686).

Dibenzylbenzenes, $C_6H_4{<}\begin{smallmatrix}CH_2.C_6H_5\\CH_2.C_6H_5\end{smallmatrix}$. The *ortho* and *para* compounds are by-products in the formation of diphenyl methane from benzyl chloride, and methylal with benzene (p. 853). The former melts at 78°; the latter at 86°.

Dibenzoylbenzenes, $C_6H_4{<}\begin{smallmatrix}CO.C_6H_5\\CO.C_6H_5\end{smallmatrix}$, **phthalophenones, phenylene diphenyl ketones.** The ortho and para derivatives are produced by the oxidation of the corresponding dibenzylbenzenes.

The *meta* and *para* compounds may be obtained from meta- and para-phthalyl chlorides with benzene and $AlCl_3$ (p. 856):—

$$C_6H_4(COCl)_2 + 2C_6H_6 = C_6H_4(CO.C_6H_5)_2 + 2HCl,$$

whereas, the so-called orthophthalyl chloride yields diphenylphthalide.

Orthophthalophenone melts at 146°; **meta or isophthalophenone** at 100°; **terephthalophenone** at 160°. Hydroxylamine yields ketoximes with them (*Berichte*, 19, 146, 153).

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2. TRIPHENYL METHANE DERIVATIVES.

These contain three benzene nuclei attached to 1 carbon-atom:—

$(C_6H_5)_3CH$	$\begin{smallmatrix}(C_6H_5)_2\\CH_3.C_6H_4\end{smallmatrix}{>}CH$	$\begin{smallmatrix}C_6H_5\\(CH_3.C_6H_4)_2\end{smallmatrix}{>}CH.$
Triphenyl Methane.	Diphenyl-tolyl Methane.	Phenylditolyl Methane.

These are the parent hydrocarbons from which originate the rosaniline dyes, the malachite-greens, the aurines and phthaleïns. They may be synthesized by methods analogous to those employed with the diphenyl methane derivatives:—

1, from benzal chloride, $C_6H_5.CHCl_2$ (or $C_6H_5.CCl_3$) and the benzenes with zinc dust or aluminium chloride:—

$$C_6H_5.CHCl_2 + 2C_6H_6 = C_6H_5.CH(C_6H_5)_2 + 2HCl;$$

2, from benzhydrol (p. 857), and the benzenes with P_2O_5 :—

$$(C_6H_5)_2CH.OH + C_6H_6 = (C_6H_5)_2CH.C_6H_5 + H_2O;$$

3, from chloroform (or CCl_4) and benzene with $AlCl_3$:—

$$3C_6H_6 + CHCl_3 + (C_6H_5)_3CH + 3HCl.$$

A better means is the condensation of benzaldehyde with anilines (their salts) and phenols, in which we have produced amido- and phenol-derivatives of triphenyl methane (p. 867). Sulphuric acid, zinc chloride, potassium bisulphate (*Berichte*, 16, 2541), and anhydrous oxalic acid serve as reagents to induce the condensation (*Berichte*, 17, 1078).

Benzaldehyde cannot be made to condense with the benzenes by the action of sulphuric acid. This condensation only takes place, in slight degree, by the application of intense heat, and the use of zinc chloride (*Berichte*, 19, 1876). However, substituted benzaldehydes, as *m*- and *p*-nitrobenzaldehyde (also terephthaldehyde) condense very readily with benzenes by the aid of sulphuric acid, forming nitrotriphenylmethanes (*Berichte*, 21, 188; 23, 1622). For the condensations of benzaldehyde with phenols, see *Berichte*, 22, 1943.

(1) **Triphenyl Methane**, $(C_6H_5)_3CH = C_{19}H_{16}$, is the product of the reaction between benzal chloride, $C_6H_5.CHCl_2$, and mercury diphenyl, $Hg(C_6H_5)_2$, and is most easily prepared from chloroform and benzene, aided by $AlCl_3$.

Preparation.—One part of $AlCl_3$ is gradually added to a mixture consisting of one part of chloroform and five parts of benzene, and the temperature raised to 60°, until the evolution of hydrogen chloride ceases (30 hours). The product is poured into water, and the oil, which separates, is fractionated. Diphenyl methane is produced at the same time (*Annalen*, 227, 107; *Berichte*, 18, Ref. 327). It is furthermore obtained from diamido- and triamido-triphenyl methane, by dissolving the latter in sulphuric acid, introducing nitrous acid and boiling with alcohol (p. 632 and *Annalen*, 206, 152).

Triphenyl methane dissolves with difficulty in cold alcohol and glacial acetic acid, easily in ether, benzene and hot alcohol, crystallizing from the latter in shining, thin leaflets, melting at 93°, and distilling about 355°. It crystallizes from hot benzene in large prisms, containing two molecules of benzene, and melts at 75°, and when exposed to the air parts with benzene and falls into a white powder.

Bromine converts triphenyl methane (dissolved in CS_2) into the *bromide*, $(C_6H_5)_3CBr$, melting at 152° (*Berichte*, 18, Ref. 327). PCl_5 converts the carbinol into the *chloride*, melting about 105°. When heated over 200° both decompose into the halogen hydride and **Diphenylene phenyl methane**,  $\left<\begin{matrix}C_6H_4\\C_6H_4\end{matrix}\right>CH.C_6H_5$, which can also be obtained from fluorene alcohol (p. 851) and benzene by means of sulphuric acid, as well as from potassium triphenyl methane (*Berichte*, 22, Ref. 660). It melts at 146°. If the bromide be heated with mercuric cyanide to 100° the *cyanide*, $(C_6H_5)_3C.CN$, results. It melts at 127°, and if boiled with glacial acetic acid and hydrochloric acid changes to **Triphenyl-acetic Acid,** $(C_6H_5)_3.C.CO_2H$, which begins softening at 230°, and melts at 264° (*Annalen*, 194, 260). Small amounts of the acid are also obtained from trichloracetic acid and benzene with $AlCl_3$.

On boiling the bromide or chloride with water we get **Triphenylcarbinol,** $(C_6H_5)_3C.OH$, which is more readily obtained by the direct hydroxylation of triphenyl methane. This is accomplished by digesting the latter with chromic acid in a glacial acetic acid solution (*Berichte*, 14, 1944). It is very readily soluble in alcohol, ether and benzene, crystallizes in shining prisms, melting at 159°, and distilling above 360° without decomposition. ***p*-Nitro-Triphenyl Methane,** $C_6H_4(NO_2).CH(C_6H_5)_2$, is prepared from *p*-nitro benzaldehyde and benzene, aided by sulphuric acid (see above). It crystallizes in white leaflets, melting at 93°. Chromic acid, in glacial acetic acid oxidizes it to the *carbinol*, $C_6H_4(NO_2).C(OH)(C_6H_5)_2$, melting at 135° (*Berichte*, 23, 1622).

When triphenyl methane is dissolved in fuming nitric acid (sp. gr. 1.5) it forms a *p*-trinitro-derivative, $CH(C_6H_4.NO_2)_3$, which crystallizes from glacial acetic acid and hot benzene in yellow scales, and melts at 206°. Sodium alcoholate converts the nitro-compound into a deep violet-colored sodium salt (p. 861) (*Berichte*, 21, 1348). By the reduction of the nitro-groups (with zinc dust and glacial acetic acid) we obtain paraleucaniline, $CH(C_6H_4.NH_2)_3$ (p. 870). By the hydroxylation of the tertiary hydrogen atom of trinitrophenyl methane (by digestion with CrO_3 in glacial acetic acid) we get **Trinitrotriphenyl Carbinol,** $(C_6H_4.NO_2)_3C.OH$, which separates from benzene or glacial acetic acid in small, colorless crystals, melting at 172°, and when the nitro-groups are reduced (with a little zinc dust and glacial acetic acid) it is transformed into pararosaniline.

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(2) **Diphenyl-tolyl Methanes,** $(C_6H_5)_2CH(C_6H_4.CH_3)$.

The *para*-compound is obtained from phenyl-paratolyl-carbinol (p. 862) and benzene, and also from benzhydrol, $(C_6H_5)_2CH.OH$, and toluene with phosphorus pentoxide. It crystallizes in thin prisms, melts at 71°, and distils above 360°. It yields a carbinol, $C_{20}H_{18}O$, and an acid, $C_{20}H_{16}O_3$, when oxidized. The trinitro-compound of diphenyl-para tolyl methane yields on reduction of the nitro- to amido-groups, and further oxidation, bluish-violet coloring substances which differ from ordinary rosaniline (*Annalen*, 194, 264).

Isomeric **Diphenyl-meta-tolyl Methane,** $(C_6H_5)_2.CH(C_6H_4.CH_3)$, is the parent hydrocarbon of ordinary leucaniline (the triamido-compound), and is obtained from the latter by replacing the $3NH_2$ groups by hydrogen. This is effected through the diazo-compound (*Annalen*, 194, 282). It dissolves readily in ether, benzene and ligroïne, with difficulty in cold alcohol and wood-spirit; crystallizes in spherical aggregations of united prisms, melting at 59.5°, and distilling undecomposed above 360°. Oxidized with chromic acid in a glacial acetic acid solution it passes into *diphenyl-metatolyl-carbinol*, $(C_6H_5)_2C(OH)(C_6H_4.CH_3)$, melting at 150°.

It dissolves in fuming nitric acid with formation of a trinitro-derivative, yielding on reduction common leucaniline, which is oxidized (on heating with a few drops of hydrochloric acid), to rosaniline (p. 871).

Amido-derivatives of the Triphenyl Methanes.

o-**Amido-triphenyl Methane**, $(C_6H_5)_2CH(C_6H_4.NH_2)$, is obtained from benzhydrol, $(C_6H_5)_2CH.OH$, and HCl-aniline, on heating with $ZnCl_2$ to 150°. It crystallizes in leaflets, or prisms, melting at 84°. Its *dimethyl* compound, $(C_6H_5)_2CH.C_6H_4.N(CH_3)_2$, is obtained from benzhydrol and dimethyl aniline upon heating with P_2O_5, also on digesting benzophenone chloride, $(C_6H_6)_2CCl_2$, with dimethyl aniline. It crystallizes from alcohol in colorless needles or prisms, melting at 132°. It does not afford a color-base by its oxidation. (*Annalen*, 206, 144 and 155.)

p-**Amido-triphenyl Methane**, $(C_6H_6)_2CH.C_6H_4.NH_2$, is produced by reducing the *p*-nitro derivative with tin and hydrochloric acid. It crystallizes from ligroïne in small vitreous needles, melting at 84°. When its acetyl compound is oxidized and saponified it yields *p*-**Amido-triphenyl Carbinol**, $(C_6H_5)_2C(OH)C_6H_4.NH_2$, the *lowest analogue of the rosaniline bases.* It crystallizes from a mixture of ether and ligroïne in colorless warts, melting at 116°. It combines with acids (*without loss of water*) to form red colored salts. These, however, lack coloring properties. (*Berichte*, 23, 1621).

Diamido-triphenyl Methane, $C_6H_5.CH(C_6H_4.NH_2)_2$, the parent substance of *malachite-green*, is obtained from benzal chloride, $C_6H_5.CHCl_2$, and aniline with zinc dust (see below), or more easily from benzaldehyde with aniline hydrochloride on heating with zinc chloride to 120°, and boiling the first formed product with dilute sulphuric acid. If aniline sulphate be applied we get the diamido-base directly (*Berichte*, 15, 676):—

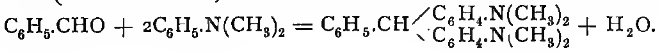
$$C_6H_5.CHO + 2C_6H_5.NH_2 = C_6H_5.CH(C_6H_4.NH_2)_2 + H_2O.$$

It is more readily obtained by boiling benzaldehyde with aniline and hydrochloric acid (*Berichte*, 18, Ref. 334). It crystallizes from benzene with 1 molecule of benzene in shining prisms or spherical aggregations, melting at 106°, and parting with benzene at 110°. The free base, crystallized from ether, melts at 139°.

It yields colorless salts with two equivalents of the acids. By their oxidation we can obtain a violet dye-stuff, *benzal violet*, with a constitution analogous to that of the rosanilines (*Annalen*, 206, 161). If the base be diazotized and boiled with water it is converted into dioxy-triphenyl-methane, $C_6H_5.CH(C_6H_4.OH)_2$; the decomposition of the diazo-compound by alkalies produces triphenyl-methane (*Annalen*, 206, 152).

On methylating diamidotriphenyl-methane by heating with methyl iodide and wood-spirit to 110° we obtain

Tetramethyl-diamido-triphenyl Methane, $C_6H_5.CH[C_6H_4.N(CH_3)_2]_2$, *leucomalachite-green*, which is obtained directly from benzaldehyde (or benzal chloride) and dimethyl aniline with zinc chloride (or oxalic acid):—

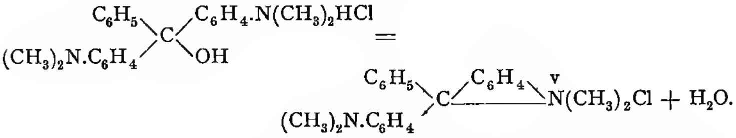


$$C_6H_5.CHO + 2C_6H_5.N(CH_3)_2 = C_6H_5.CH\begin{matrix}\diagup C_6H_4.N(CH_3)_2 \\ \diagdown C_6H_4.N(CH_3)_2\end{matrix} + H_2O.$$

Leucomalachite-green is dimorphous, and crystallizes in leaflets, melting at 93–94°, or in needles, which melt at 102°. The first modification is obtained pure by crystallization from alcohol, the second from benzene. It yields colorless salts with two equivalents of the acids, and with two molecules of methyl iodide forms an ammonium iodide. The free base oxidizes, even in the air, more readily by oxidizing agents (manganese dioxide and dilute sulphuric acid in the cold, lead dioxide and hydrochloric acid, or chloranil) and becomes

Tetramethyl-diamido-triphenyl Carbinol, $C_6H_5.C(OH)[C_6H_4.N(CH_3)_2]_2$, which is the basis of malachite-green. It is obtained from its salts (malachite-green) by precipitation with the alkalies. Free carbinol crystallizes from ligroïne in colorless needles or spherical aggregations, melting at 130°, and decomposes on stronger heating. Reduction with zinc and hydrochloric acid converts it again into leucomalachite-green.

The free base yields almost colorless solutions with acids in the cold; upon standing, more rapidly on heating, the solution acquires a green color and then contains the green salts—*malachite-greens*—of the anhydro-base. It is very probable that amine salts (O. and E. Fischer) of the carbinol are first produced, but by an inner condensation water is eliminated and they change to dye-salts (malachite-greens) (*Berichte*, 12, 2348) free from oxygen:—



Of these salts the double salt with zinc chloride, $3(C_{23}H_{25}N_2.Cl)2ZnCl_2 + 2H_2O$, and the oxalate, $2C_{23}H_{24}N_2.3C_2H_2O_4$, form the commercial *malachite-green* or *Victoria green*. They are mostly soluble in water, and crystallize in large, greenish prisms or plates. The alkalies precipitate the colorless carbinol base from its salts. *Malachite-green* and *brilliant green* (see below) color silk and wool, from feeble acid baths, an intense green. This also occurs with cotton mordanted with tannin and alumina, or tannin and tartar emetic.

Malachite-green is obtained by oxidizing leucomalachite-green, prepared from benzaldehyde (p. 867), hence called *aldehyde green* (O. Fischer); or more directly, though less advantageously, on heating benzo-trichloride with dimethyl aniline and zinc chloride (Doebner):—

$$C_6H_5.CCl_3 + 2C_6H_5.N(CH_3)_2 = C_{19}H_{13}(CH_3)_4N_2Cl + 2HCl.$$

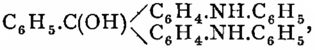
Since success has attended the efforts made to prepare benzaldehyde the first process has been almost exclusively followed in the technical preparation of the color.

Benzoyl chloride, $C_6H_5.CO.Cl$, and benzoic anhydride (*Annalen*, 206, 137) are similarly condensed with dimethyl aniline to malachite-green.

Benzaldehyde forms perfectly analogous green color substances with diethyl aniline and methyl diphenylamine, $(C_6H_5)_2N.CH_3$. The dye-substance obtained from diethyl aniline shows a yellow-tinted green color. Its sulphate or zinc-chloride double salt constitutes what in commerce is known as *brilliant green* or *solid green* (new Victoria green). Dichlorbenzaldehyde, $C_6H_3Cl_2.CHO$, and dimethyl- and diethyl-anilines yield dyes, which are applied as *indigo substitutes* (instead of the mixed greens derived from indigo). By condensing benzaldehyde and benzyl-ethyl aniline, $C_6H_5.N(CH_3).CH_2.C_6H_5$, and introducing sulphur into the product, the *light greens, guinea green* or *acid green* (*Berichte*, 22, 588) are produced; they show the same color in artificial light.

It reacts in the same way with ortho- and meta-dimethyl toluidine, whereas no condensation product is furnished by the para-dimethyl toluidine. The base from meta-toluidine does not yield a coloring substance when oxidized (*Annalen*, 206, 140). Salicylic aldehyde and paraoxybenzaldehyde afford green coloring substances. Furthermore, *nitromalachite-greens* have been prepared from meta-, para-, and ortho-nitrobenzaldehydes with dimethyl aniline. They are perfectly analogous to ordinary malachite-green (*Berichte*, 15, 682). See *Berichte*, 22, 3207, for the condensations with toluidines.

The **Diphenyl-diamido-triphenyl Carbinol,**



$$C_6H_5.C(OH)\begin{cases}C_6H_4.NH.C_6H_5\\C_6H_4.NH.C_6H_5\end{cases},$$

obtained from diphenylamine and benzo-trichloride, and called *viridin*, readily yields a sulpho-acid. The alkali salts of this acid constitute the so-called *alkali green* (*Berichte*, 15, 1580).

By heating leucomalachite green with sulphuric acid and then further oxidizing, or by directly introducing sulphur into malachite green, *sulpho-acids* result; their sodium salts are applied under the names *Helvetia green* or *acid green.*

Para-nitro-diamido-triphenyl Methane, like diamido-triphenyl methane (p. 867), is obtained from paranitrobenzaldehyde and aniline sulphate when heated with zinc chloride:—

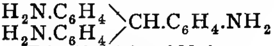
$$C_6H_4(NO_2).CHO + 2C_6H_5.NH_2 = \underset{\text{Paranitro-diamido-triphenyl Methane.}}{C_6H_4(NO_2).CH(C_6H_4.NH_2)_2} + H_2O.$$

On reduction with zinc and acetic acid this yields triamido-triphenyl methane, $(C_6H_4.NH_2)_3CH$, *paraleucaniline.*

Meta-nitro-diamido-triphenyl Methane, similarly obtained from *m*-nitrobenzaldehyde, melts at 136°, and by reduction yields pseudo-leucaniline, $CH(C_6H_4.NH_2)_3$, isomeric with paraleucaniline; in it the amido-group assumes the meta-position in one benzene nucleus, whereas, in all other diamido- and triamido-triphenyl methanes, the amide groups occupy the para-position (p. 870). It oxidizes to a violet coloring substance. Ortholeucaniline, from *o*-nitro-benzaldehyde, is oxidized to a brown coloring substance (*Berichte*, 16, 1305; 17, 1889).

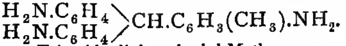
Benzaldehyde and nitrobenzaldehydes also condense with *o*- and *p*-toluidine (*Berichte*, 18, 2094), whereas metatoluidine and aniline meta-derivatives only react with ease, provided that the amido-group is methylated (*Berichte*, 20, 1563).

TRIAMIDO-TRIPHENYL METHANES. ROSANILINES.



$$\begin{matrix}H_2N.C_6H_4\\H_2N.C_6H_4\end{matrix}\Big\rangle CH.C_6H_4.NH_2$$

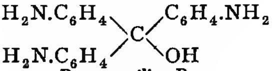
Triamido-triphenyl Methane, Paraleucaniline.



$$\begin{matrix}H_2N.C_6H_4\\H_2N.C_6H_4\end{matrix}\Big\rangle CH.C_6H_3(CH_3).NH_2.$$

Triamido-diphenyl-tolyl Methane, Leucaniline.

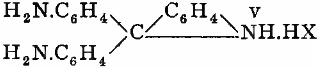
The rosaniline coloring substances are produced from these in a manner similar to the derivation of *benzal violet* and *malachite green* from diamidotriphenyl methane (p. 867). The carbinols or free *rosaniline bases* result when they are oxidized (adding hydroxyl to the CH-group):—



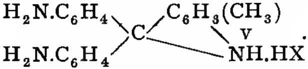
Pararosaniline Base.

Rosaniline Base.

These alone are colorless, but yield salts with the acids by exit of water (analogous to the malachite-green base) and form the *rosaniline dye-substances.* E. and O. Fischer contend that the salt is produced as follows: an exit of water occurs, followed by a peculiar linking of the C-atom to an N-atom in the para-position, forming a chromogenic group which imparts to the rosanilines their dyeing properties (*Berichte,* 12, 2350):—



Para-rosaniline Salt.



Rosaniline Salt.

By the replacement of the hydrogen of the amido-groups in the salts by alkyls or phenyls, the different colored rosaniline dyes result. The common and first discovered rosanilines are derived from diphenyl-meta-tolyl methane, $C_{20}H_{18}$ (p. 866), and the carbinol base, $C_{20}H_{20}(OH)N_3$, and can also be called salts of the anhydride base, $C_{20}H_{19}N_3$; the latter is unstable in a free state, and when liberated from its salts by alkalies, absorbs water and changes immediately to the carbinol base. The derivatives of triphenyl methane, $C_{19}H_{16}$, and of the base, $C_{19}H_{18}(OH)N_3$ or $C_{19}H_{17}N_3$ are termed pararosanilines, to distinguish them from those rosanilines just mentioned. The *colorless* salts obtained by the reduction of the rosanilines form bases, $C_{19}H_{19}N_3$ and $C_{20}H_{21}N_3$, called *leucanilines.*

Triamido-triphenyl Methane, $C_{19}H_{19}N_3 = CH(C_6H_4.NH_2)_3$, **Paraleucaniline,** is obtained from trinitro-triphenyl methane (p. 866) and from para-nitro-diamidotriphenyl methane (p. 869) by reduction with zinc dust and acetic acid, also from para-rosaniline with zinc dust and hydrochloric acid, and by heating *p*-amidobenzaldehyde and dimethylaniline with zinc chloride:—

$$C_6H_4(NH_2).CHO + 2C_6H_5.NH_2 = CH(C_6H_4.NH_2)_3 + H_2O.$$

It is thrown out of its salts as a white flocculent precipitate. When its diazo-compound, $C_{19}H_{13}(N_2Cl)_3$, is decomposed by alcohol, it yields triphenyl methane, $C_{19}H_{16}$. Pararosaniline is the oxidation product of para-leucaniline. Pseudo-leucaniline affords a violet, and ortho-leucaniline a brown coloring substance when oxidized (p. 870).

Pararosaniline. The free base, $C_{19}H_{19}N_3O = (NH_2.C_6H_4)_3C.OH$, or its salts, $C_{19}H_{17}N_3.HX$ (see above), result in the oxidation of para-leucaniline and in the reduction of trinitrophenyl carbinol (p. 866), with a little zinc dust and glacial acetic acid. It is most easily made by oxidizing a mixture of aniline and paratoluidine by arsenic acid (p. 872). In its properties and derivatives it is perfectly analogous to rosaniline. Its diazochloride, $C_{19}H_{12}(OH)N_6Cl_3$, yields *aurine*, $C_{19}H_{14}O_3$, when boiled with water.

In para-rosaniline and in para-leucaniline the amide groups in the three benzene nuclei occupy the para-position (referred to the point of union of the methane carbon). We infer this from the synthetic methods (from para-nitrobenzaldehyde and para-amidobenzaldehyde) and from their relations to the aurines and to para-dioxybenzophenone (p. 860) (*Berichte*, 14, 330). It is very probable that common rosaniline contains its amide-groups in the same position; as it is obtained by means of ortho-toluidine the methyl in it occupies the meta-position referred to the methane carbon. See *Berichte*, 22, 2573 as to the influence exerted by side-groups upon the dye-character of the rosanilines.

Triamido-diphenyl-tolyl Methane, Leucaniline, $C_{20}H_{21}.N_3 = (NH_2.C_6H_4)_2CH.C_6H_3(CH_3).NH_2$, is obtained by the reduction of trinitro-diphenyl meta-tolyl methane (p. 866), and is obtained by digesting the fuchsine salts with ammonium sulphide, or zinc dust and hydrochloric acid. The alkalies throw it out from its salts as a white, flocculent precipitate, which separates from water in small crystals. It yields colorless crystalline salts with three equivalents of acid. By diazotizing and replacing the diazo-groups by hydrogen (best by dissolving in concentrated sulphuric acid, conducting nitrous acid into the same, and boiling with alcohol, p. 632), leucaniline is changed into diphenyl-meta-tolyl methane. Oxidizing agents convert it into rosaniline (its salts).

The oxidation of the leucanilines to rosanilines succeeds best when they are heated with a concentrated arsenic acid solution, or with metallic oxides to 130—140°, or by boiling the alcoholic solution with chloranil. Paraleucaniline and common leucaniline are also converted into coloring substances by heating them with a few drops of hydrochloric acid upon a platinum foil. This behavior rapidly distinguishes the second from some isomerides (*Annalen*, 194, 284).

Rosaniline, $C_{20}H_{21}N_3O$. The rosaniline salts, $C_{20}H_{19}N_3.HX$ (p. 870), are obtained in the oxidation of leucaniline, and are technically prepared by oxidizing a mixture of aniline and ortho- and para-toluidine (see below). Alkalies precipitate the *free base* (the carbinol), $C_{20}H_{21}N_3O$, from the salt solution; it crystallizes from alcohol and hot water in colorless needles or plates. It reddens on exposure, and when heated suffers decomposition. Its diazo-compounds, *e. g.*, $C_{20}H_{14}(OH)N_6Cl_3$, are produced when nitrous acid acts on the rosaniline salts, and when boiled with water they afford rosolic acid, $C_{20}H_{16}O_3$.

Free rosaniline, $C_{20}H_{21}N_3O$, is a base, which will expel ammonia from the ammonium salts. It combines with one and three equivalents of acids, undergoing an anhydride formation (p. 870), and yields salts, *e. g.*, $C_{20}H_{19}N_3.HCl$ and $C_{20}H_{19}N_3.3HCl + 4H_2O$. The latter are yellow-brown in color and not very stable; water decomposes them into the stable, *monacid* salts with intense colors. These are applied as dyes. They are most readily soluble in water and alcohol, and crystallize readily in metallic, greenish crystals. Their solutions are carmine red in color, and stain animal tissue directly violet-red, while vegetable fibre (cotton) must first be mordanted (tannin). The commercial *fuchsine* (magenta) consists chiefly of the hydrochloride or acetate, $C_{20}H_{19}N_3.C_2H_4O_2$. The fatty acid salts, insoluble in water and produced by dissolving the free rosaniline base in fatty acids, are employed in decorative printing.

All the rosanilines are changed to colorless leucanilines when treated with reducing agents (heating to 120° with ammonium sulphide). When heated to 200° with hydrochloric or hydriodic acid, the rosanilines are broken up into their component anilines. Upon boiling with hydrochloric acid pararosaniline breaks down into aniline and diamidobenzophenone (p. 859), and rosaniline into toluidine and diamidobenzophenone.

Preparation.—Technically the rosaniline salts are obtained by oxidizing aniline oil (a mixture of aniline with para- and ortho-toluidine) with metallic salts (tin chloride, mercuric nitrate) or more advantageously with arsenic acid. If pure aniline be employed no coloring substance is formed. When pure aniline and paratoluidine are used pararosaniline results:—

$$2C_6H_5.NH_2 + \underset{\text{Paratoluidine.}}{C_7H_7.NH_2} + 3O = \underset{\text{Pararosaniline.}}{C_{19}H_{17}N_3O} + 2H_2O;$$

whereas common rosaniline is obtained from aniline, paratoluidine and orthotoluidine (*Berichte*, 13, 2204; 15, 2367):—

$$C_6H_5.NH_2 + 2C_7H_7.NH_2 + 3O = \underset{\text{Rosaniline.}}{C_{20}H_{21}N_3O} + 2H_2O.$$

The reaction probably occurs in such a manner that para-amido benzaldehyde is first produced from the paratoluidine, and this then (like para-nitrobenzaldehyde, p. 869) condenses with two aniline molecules to the leuco-bases:—

$$NH_2.C_6H_4.CHO + 2C_6H_5.NH_2 = NH_2.C_6H_4.CH(C_6H_4.NH_2)_2 + H_2O,$$

which further oxidizes to rosaniline.

An interesting formation of pararosaniline is that of heating aniline with carbon tetrachloride to 230° when the latter furnishes the linking carbon atom, and there ensues a reaction analogous to that of the formation of triphenyl methane from benzene and CCl_3H or CCl_4 (865). The hydroiodide of pararosaniline results by using iodoform, CHI_3 (Caro).

In the preparation of rosaniline according to the *arsenic acid method* (Girard and Medloc) aniline oil, or better, the proper mixture of aniline and toluidine is heated to 180-200° for 7–10 hours with a concentrated arsenic acid (¾ part) solution in iron retorts with agitators until the mass assumes a metallic lustre. The product, consisting chiefly of rosaniline arsenite, is extracted with water and filtered. When the solution cools a violet dye-substance separates, and upon the addition of common salt rosaniline hydrochloride crystallizes out. The crystals thus obtained contain arsenic, but are freed from it by repeated crystallizations.

According to another method (by Coupier) applied technically, the oxidizing agent is either nitrobenzene or nitrotoluene.

To obtain red, heat aniline oil (a mixture of aniline, *p*- and *o*-toluidine), one half of it being converted into hydrochloride, with 50 per cent. nitrobenzene and a little ferrous chloride or ammonium vanadate to 180–190° in an oil bath. Extract the rosaniline hydrochloride with water. In these changes the nitrobenzene acts as an oxidizer, and does not take part in the formation of the rosaniline (Lange, *Berichte*, 18, 1918).

The commercial dyestuffs, obtained as described, are really salts of rosaniline, $C_{20}H_{19}N_3$, and apparently contain, although in slight quantity, salts of pararosaniline, $C_{19}H_{17}N_3$, and the homologous base, $C_{21}H_{21}N_3$. In addition to the rosaniline the fusion also contains other violet and brown dyes, such as mauveïn (viol-aniline), an azine dyestuff, and chrysaniline, an acridine derivative. The *fuchsine* absolutely free from arsenic, which is obtained from it by a transposition with sodium chloride, is called *rubine.* Salt precipitates red-brown dye-substances from the mother liquors.

Verguin (1859) first prepared rosaniline upon a large scale and introduced it into commerce under the name fuchsine. A. W. Hofmann has studied it scientifically since 1861; he proved the fuchsine salts to be salts of a base $C_{20}H_{19}N_3.H_2O$. The true constitution of the rosanilines—the proof that they were derivatives of triphenylmethane—was demonstrated analytically and synthetically by Emil and Otto Fischer (1876, *Annalen*, 194, 242), although preliminary investigations in this direction had been previously made by Caro and Graebe. (*Berichte*, 11, 1116, 1348).

Alkylic Rosanilines.

When the rosaniline salts are heated with alkyl iodides or chlorides (and the alcohols) the hydrogen of the amido-groups can be replaced by alkyls. Of the trialkylic compounds—

$$C_{20}H_{17}(OH)N_3(CH_3)_3 \text{ and } C_{20}H_{17}(OH)N_3(C_2H_5)_3,$$

resulting in this manner, the methyl base yields reddish-violet-colored salts and the ethyl base pure violet salts (Hofmann's Violet, Dahlia); these dissolve with difficulty in water, but dissolve easily in alcohol.

The introduction of more methyl affords higher methylated dyes until hexamethyl rosaniline is reached; its color changes with the number of methyl groups, from red to violet.

Hexamethyl-rosaniline is capable of uniting with CH_3I (1 molecule) to form a *green* colored salt $C_{20}H_{14}N_3(CH_3)_6I.CH_3I$, that at 120° again eliminates methyl iodide and yields a bluish violet iodide, $C_{20}H_{14}N_3.(CH_3)_6I$. The picrate, a dark green powder, and the crystalline $ZnCl_2$-double salt, readily soluble in water, constituted the *iodide green* or *night green* of commerce, but at present are supplanted by the cheaper methyl- and malachite-greens.

Similarly, hexamethyl pararosaniline, $C_{19}H_{12}(OH)N_3(CH_3)_6$ (methyl violet, see below), when heated with methyl chloride (methyl iodide or methyl nitrate) yields so-called *methyl green;* its hydrochloride, $C_{19}H_{12}N_3Cl(CH_3)_6(CH_3Cl)$, as the zinc chloride double salt, forms the commercial dye. It occurs as a bright gold and green mass. At 100-120° methyl green loses methyl chloride and becomes violet. At present both are almost entirely replaced by malachite green.

Aldehyde green, another green rosaniline dye, has been prepared by heating rosaniline with aldehyde and sulphuric acid, and by further action of sodium hyposulphite. It is very probably a quinaldine (*Berichte*, 19, 749).

The phenylated rosanilines are obtained by heating rosaniline hydrochloride with aniline or toluidines (p. 603), or the free base with aniline and some benzoic acid. The triphenyl-rosaniline hydrochloride, $C_{20}H_{16}(C_6H_5)_3N_3.HCl$, appeared in commerce as *aniline blue,* a bluish-brown crystalline powder with copper lustre, soluble in alcohol but not in water. To dissolve it in the latter sulpho-salts are prepared, which exhibit different shades of blue (*soluble blue*) corresponding to the number of sulpho-groups in them. At present diphenylamine blue and other dyes have taken its place. Diphenylamine results on distilling triphenyl-rosaniline.

Pararosaniline Derivatives. Instead of first preparing rosaniline and then adding alkyl, it was suggested that the same compounds could be obtained by directly oxidizing alkyl anilines (dimethyl aniline, diphenylmethylamine). The resulting dyes, according to their method of preparation, are derivatives of pararosaniline, $C_{19}H_{17}N_3$. They are obtained by oxidizing trimethyl aniline upon digesting it with copper chloride (or copper sulphate) and potassium chlorate at 50–60°. On a small scale the oxidation is best effected by means of chloranil, $C_6Cl_4O_2$ (p. 701). The reaction very likely proceeds as follows: A methyl group splits off and is oxidized to formic aldehyde, which then condenses three molecules of the alkyl anilines:—

$$CH_2O + 3C_6H_5.N(CH_3)_2 + O_2 = C(OH)[C_6H_4.N(CH_3)_2]_3 + 2H_2O.$$

The *methyl violet* thus formed occurs in commerce in the form of hydrochloride, an amorphous bright green mass, easily soluble in water and alcohol. It consists chiefly of penta- and hexamethyl-rosaniline, and also contains the tri- and tetramethyl compounds, which are separated by fractional crystallization with difficulty

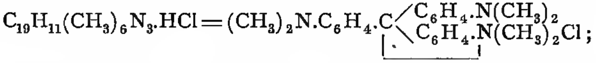
(*Berichte*, **19**, 107). As the number of methyl groups increases the violet color assumes a deeper blue tint.

The following methyl derivatives have been obtained in a pure state:—

Tetra-methyl Para-leucaniline, $H_2N.C_6H_4.CH{<}\substack{C_6H_4.N(CH_3)_2\\ C_6H_4.N(CH_3)_2}$, is obtained by reducing *p*-nitro-malachite-green (p. 869), formed from para-nitrobenzaldehyde and dimethyl aniline. It melts at 152°. It is oxidized to **Tetra-methyl Violet,** $C_{19}H_{13}(CH_3)_4N_3.HCl$. The acetate of paraleucaniline may be oxidized to a green dye (a malachite-green, as one NH_2-group is linked by acetyl) (*Berichte*, **16**, 708).

Pentamethyl-para-leucaniline, $C_{19}H_{14}(CH_3)_5N_3$, has been obtained from the reduction product of commercial methyl violet (a mixture of penta- and hexa-methyl violet) by means of the acetate. It melts at 116°, and when oxidized yields **Penta-methyl Violet,** $C_{19}H_{12}(CH_3)_5N_3.HCl$. When its *acetate* is oxidized it yields a green dye (*Berichte*, **16**, 2906).

Hexamethyl-paraleucaniline, $C_{19}H_{13}(CH_3)_6N_3$, *Leuco-violet*, is obtained pure on heating ortho-formic ester, $CH(O.C_2H_5)_3$, with dimethyl aniline (3 molecules) and zinc chloride, and from tetramethyldiamidobenzophenone (p. 859) with dimethyl aniline and PCl_3. If separated from its HCl-salt it crystallizes in silvery leaflets, and melts at 173°. If oxidized it yields **Hexamethyl Violet**:—



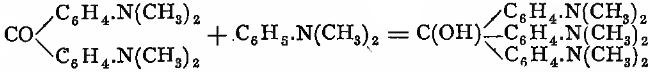
$$C_{19}H_{11}(CH_3)_6N_3.HCl = (CH_3)_2N.C_6H_4.C{<}\substack{C_6H_4.N(CH_3)_2\\ C_6H_4.N(CH_3)_2Cl}\ ;$$

this possesses a blue tint. Its carbinol base, $C_{19}H_{12}(OH)N_3(CH_3)_6$, crystallized from ether, melts at 195°.

All three leucanilines yield the iodo-methylate, $C_{19}H_{13}(CH_3)_6N_3.3CH_3I$, when they are heated with much methyl iodide and methyl alcohol. This melts at 185°, and heated to 130° regenerates hexamethyl-para-leucaniline.

The methyl violets are reduced to leuco-compounds when heated to 120° with ammonium sulphide. Protracted boiling with hydrochloric acid causes them to lose one molecule of dimethylaniline and break down. Thus from pentamethyl violet we obtain trimethyl-diamidobenzophenone, $CO{<}\substack{C_6H_4.NH.CH_3\\ C_6H_4.N(CH_3)_2}$, and from hexamethyl violet, tetramethyldiamido-benzophenone (p. 859) (*Berichte*, **19**, 108).

Pure hexamethyl pararosaniline, distinguished from the lower methyl derivatives by great power of crystallization and the blue color of its salts, hence called *Crystal Violet*, is produced on a large scale by the condensation of tetramethyldiamidobenzophenone (from dimethyl aniline and $COCl_2$, p. 859) with dimethyl aniline:—



$$CO{<}\substack{C_6H_4.N(CH_3)_2\\ C_6H_4.N(CH_3)_2} + C_6H_5.N(CH_3)_2 = C(OH)\begin{cases}C_6H_4.N(CH_3)_2\\ C_6H_4.N(CH_3)_2.\\ C_6H_4.N(CH_3)_2\end{cases}$$

It may therefore be directly obtained by heating dimethylaniline with $COCl_2$ and $AlCl_3$ or $ZnCl_2$ (*Berichte*, **18**, 767; Ref. 7). Formic acid, formic ester, chlorcarbonic ester, perchlormethyl mercaptan, $CSCl_2$, etc., act the same as phosgene.

Tetramethyl-diamido benzophenene condenses similarly with other bases. It yields with phenyl-α-napthylamine, $C_6H_5.NH.C_{10}H_7$, *tetramethyl-naphthyl-rosaniline*, $C(OH){<}\begin{matrix}[C_6H_4.N(CH_3)_2]_2\\ C_6H_4.NH.C_{10}H_7\end{matrix}$. The zinc chloride double salt of the latter is **Victoria Blue**, used for cotton dyeing (see *Berichte*, **22**, 1888).

Diphenylamine Blue can be obtained by heating diphenylamine, $(C_6H_5)_2HN$, with carbon hexachloride, C_2Cl_6, or oxalic acid, to 120°. It is identical with *triphenyl-pararosaniline*, $C(OH)(C_6H_4.NH.C_6H_5)$ (*Berichte*, 23, 1964), obtained by the action of aniline upon pararosaniline. At present it is only the sodium salts of its mono- and disulpho-acids that are applied as *Alkali Blue* and *Water Blue* in dyeing.

Perchlorformic ester, $CClO_2CCl_3$, in a similar manner converts diphenyl methylamine, $(C_6H_5)_2N.CH_3$, into *trimethyl-triphenyl-pararosaniline*, $C(OH)\left(C_6H_4.N{<}\begin{matrix}CH_3\\ C_6H_5\end{matrix}\right)_3$ (*Berichte*, **19**, 278). Phosgene converts triphenylamine into the hydrochloride of *hexaphenyl pararosaniline*, $C(OH)[C_6H_4.N(C_6H_5)_2]_3$ (*Berichte*, **19**, 758). *Tricarbazol Carbinol*, $C(OH)(C_{12}H_7NH)_3$ (*Berichte*, **20**, 1904), is produced by heating together carbazol and oxalic acid (*Berichte*, **20**, 1904). It is analogous to the triphenylamine derivative.

By converting rosaniline, by means of the tridiazo-compound into the *trihydrazine* derivative, there results *Roshydrazine*, $C(OH)(C_6H_5.NH.NH_2)_3$; this by condensation with aldehydes and ketones yields red and blue dyestuffs (*Berichte*, **20**, 1557).

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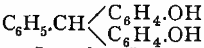
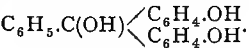
2. PHENOL DERIVATIVES OF THE TRIPHENYL METHANES.

These possess a constitution perfectly analogous to that of the amido-derivatives, as they contain hydroxyls in the positions held by the amido-groups. They are synthetically produced in a similar manner by the condensation of the phenols, and on the other hand may be obtained from the amido-compounds by means of the diazo-derivatives. Their leuco-derivatives (p. 870), are oxidized to carbinols, $R_3C.OH$, having usually the properties of a dye-substance. Those compounds, in which but two benzene nuclei are hydroxylated, and which correspond to the diamido or malachite-green compounds, are termed *benzeïnes*, whereas the derivatives with three hydroxylated benzene nuclei are called *aurines* or *rosolic acids*:—



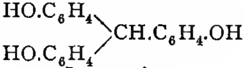
$$C_6H_5.CH{<}\begin{matrix}C_6H_4.OH\\ C_6H_4.OH\end{matrix}$$

Leuco-benzeïne.



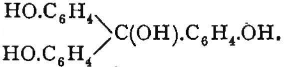
$$C_6H_5.C(OH){<}\begin{matrix}C_6H_4.OH\\ C_6H_4.OH\end{matrix}.$$

Benzeïne.



$$\begin{matrix}HO.C_6H_4\\ HO.C_6H_4\end{matrix}{>}CH.C_6H_4.OH$$

Leuco-aurine.



$$\begin{matrix}HO.C_6H_4\\ HO.C_6H_4\end{matrix}{>}C(OH).C_6H_4.OH.$$

Aurine.

Benzeïnes.

Dioxy-triphenyl Methane, $C_{19}H_{16}O_2 = C_6H_5.CH(C_6H_4.OH)_2$, leucobenzeïne, formerly called leucobenzaurine, is obtained from diamido-triphenyl methane (p. 867), with nitrous acid and by reducing benzaurine with zinc and hydrochloric acid as well as by the condensation of benzaldehyde and phenol (2 molecules) with sulphuric acid (*Berichte*, 22, 1944). It crystallizes from dilute alcohol in yellow needles or prisms, melting at 161°. When oxidized it yields benzeïne.

Dioxy-triphenyl Carbinol, $C_{19}H_{16}O_3 = C_6H_5.C(OH)(C_6H_4.OH)_2$, *Phenol Benzeïne*, is only stable as an *anhydride*, $C_{19}H_{14}O_2$, formerly called *benzaurine*. It is produced in the condensation of benzotrichloride and phenol (similar to the formation of malachite-green) (*Doebner*, *Annalen*, 217, 223):—

$$C_6H_5.CCl_3 + 2C_6H_5.OH + H_2O = C_{19}H_{16}O_3 + 3HCl.$$

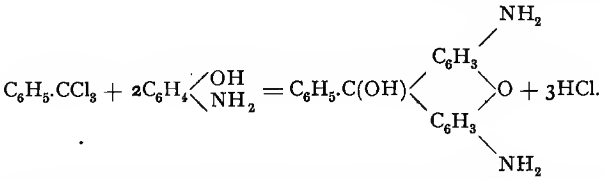
All mono- and polyhydric phenols, in which the para position with reference to a hydroxyl group is not substituted, *e. g.*, *o*- and *m*-cresol, α-naphthol, resorcinol and pyrocatechin (but not *p*-cresol, β-naphthol, hydroquinone etc.) (*Berichte*, 23, Ref. 340), react in the same manner with the formation of benzeïnes.

The benzeïnes are generally red-colored compounds with metallic lustre. They dissolve on boiling with sodium bisulphite; acids reprecipitate them. Alkalies dissolve them with the formation of red or violet-colored salts. The carbon dioxide of the air decomposes the latter.

Phenol benzeïne (see above) breaks down, when fused with alkalies, into benzene and dioxybenzophenone, and this latter decomposes further into paraoxybenzoic acid and phenol. The other benzeïnes react similarly.

α-Naphthol Benzeïne, $2\left(C_6H_5.C(OH)\begin{matrix}\diagup C_{10}H_6.OH \\ \diagdown C_{10}H_6.OH\end{matrix}\right) - H_2O$, from benzotrichloride and naphthol (*Annalen*, 257, 58), dissolves with a dark green color, in alkalies; acids color it reddish-yellow. It is extensively employed as a delicate *indicator* (*Chem. Zeitschr.*, 1890, 605).

The benzeïnes, from phenols, possess but feeble dyeing properties, as their alkali salts are even decomposed by carbon dioxide. On the other hand the *diamidobenzeïnes* from benzotrichloride and *m*-amidophenols, combining the benzeïne character with that of the malachite greens, are called *rosamines*, and in their salts with acids are very intense, true dyestuffs (*Berichte*, 22, 3001):—



$$C_6H_5.CCl_3 + 2C_6H_4\begin{matrix}\diagup OH \\ \diagdown NH_2\end{matrix} = C_6H_5.C(OH)\begin{matrix}\diagup C_6H_3(NH_2) \diagdown \\ \diagdown C_6H_3(NH_2) \diagup\end{matrix}O + 3HCl.$$

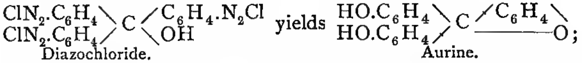
In a similar manner, dimethyl and-diethyl-*m*-amidophenol yield *tetramethyl*- and *tetraethyl-rosamines*, which find application as violet red dye substances. They are strongly fluorescent.

AURINES AND ROSOLIC ACIDS.

These compounds correspond perfectly to the rosanilines. They contain three hydroxylated benzene nuclei (p. 876) and in the free state are peculiar carbinol anhydrides. They are incompletely fixed by the fibre of the material and are only applied in the form of lakes.

Trioxy-triphenyl Methane, $C_{19}H_{16}O_3 = CH(C_6H_4.OH)_3$, **Leucaurine**. This is obtained in the reduction of aurine, its carbinol anhydride, by means of zinc dust. It dissolves in alcohol and acetic acid, and crystallizes in colorless needles, which become colored on exposure to the air.

Aurine, $C_{19}H_{14}O_3$ (para-rosolic acid), is produced on boiling the diazo-hydrochloride of pararosaniline with water, when the carbinol formed at first splits off water (*Annalen*, 194, 301):—



$$\left.\begin{array}{l}ClN_2.C_6H_4\\ClN_2.C_6H_4\end{array}\right\rangle C\left\langle\begin{array}{l}C_6H_4.N_2Cl\\OH\end{array}\right. \text{ yields } \left.\begin{array}{l}HO.C_6H_4\\HO.C_6H_4\end{array}\right\rangle C\begin{array}{l}\diagup C_6H_4\diagdown\\ \overline{\qquad\qquad} O;\end{array}$$

Diazochloride. Aurine.

also by the condensation of dioxybenzophenone chloride (from *p*-dioxybenzophenone, p. 860) with phenol:—

$$CCl_2(C_6H_4.OH)_2 + C_6H_5.OH. = C_{16}H_{14}O_3 + 2HCl,$$

and by the condensation of phenol with formic acid on heating with zinc chloride. It is made by heating phenol with oxalic and sulphuric acids; the combining carbon atom is derived from the oxalic acid.

The method of Kolbe and Schmitt (1861) is that technically employed for the manufacture of aurine or yellow corallin. It consists in heating phenol (1 part) and anhydrous oxalic acid (⅔ part) with sulphuric acid (½ part) to 130–150°, until the liberation of gas ceases (*Annalen*, 202, 185). On extracting with water there remains a resinous metallic green mass which forms a yellow powder. It contains, besides aurine, various other, quite similar, substances, from which the first can be separated either by means of sulphurous acid (*Annalen*, 194, 123), or by precipitation as aurine-ammonia, when NH_3 is conducted into the alcoholic solution (*Annalen*, 196, 177).

Aurine dissolves in glacial acetic acid and alcohol, crystallizes in dark red needles or prisms with metallic lustre, and decomposes when heated above 220°. Acids precipitate it from the alkaline fuchsine-red solutions. When ammonia is conducted into the alcoholic solution, the ammonium salt, $C_{19}H_{12}(NH_4)_2O_3$, separates in dark red needles with a steel-blue lustre. With the primary alkaline sulphites it also yields colorless, crystalline derivatives, decomposable by acids and alkalies. Aurine forms crystalline compounds with hydrochloric acid. Water decomposes them. Digested with zinc dust and hydrochloric acid or acetic acid, aurine is reduced to leucaurine, $C_{13}H_{16}O_9$. Heated to 250° with water it breaks up into dioxybenzophenone and phenol:—

$$C_{19}H_{14}O_3 + H_2O = CO(C_6H_4.OH)_2 + C_6H_5.OH.$$

Aurine is changed to pararosaniline when it is heated with aqueous ammonia to 150°. An intermediate product (having 1 or 2 amide groups) is the so-called *Peonine* (red corallin). With aniline we obtain triphenyl-rosaniline, and the intermediate product is *Azuline*.

Leuco-rosolic Acid, $C_{20}H_{18}O_9 = (HO.C_6H_4)_2.CH.C_6H_3(CH_3).OH$, trioxy-diphenyl-tolyl methane, and **Rosolic Acid**, $C_{20}H_{16}O_3$, corresponding to leucoaniline and rosaniline, are constituted similarly to leucaurine and aurine, and resemble them in all their reactions. Rosolic acid, like aurine, is obtained by boiling the diazochloride of rosaniline with water and by oxidizing a mixture of phenol and cresol, $C_6H_4(CH_3)OH$, with arsenic acid and sulphuric acid, whereby the linking methane carbon is furnished by the methyl group. When rosolic acid is digested with alcohol and zinc dust, it is reduced to leucorosolic acid.

The so-called *Pittical* belongs to the aurine series. It was first obtained in oxidizing the fractions of beech-wood tar, boiling at high temperatures. It consists of the dark blue salts of *Eupittonic acid* (Eupitton), which, in its uncombined state, shows an orange-yellow color. It can be synthesized (analogous to rosolic acid) by oxidizing a mixture of the dimethyl ester of pyrogallic acid and methyl pyrogallic acid (p. 695):—

$$2C_6H_3\begin{cases}(O.CH_3)_2\\OH\end{cases} + C_6H_2(CH_3)\begin{cases}(O.CH_3)_2\\OH\end{cases} = C_{25}H_{26}O_9 + 3H_2.$$

Eupitton is, therefore, an aurine, into which six methoxyl groups have been introduced (comp. *Berichte*, 21, 1371):—

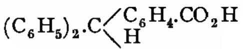
$$C_{25}H_{26}O_9 = C_{19}H_8(O.CH_3)_6O_3.$$

Eupitton forms orange-yellow crystals, melting with decomposition at 200°. It dissolves with a deep blue color in alkalies yielding salts, which are precipitated by excess of alkali. When heated with ammonia it suffers a replacement of its hydroxyls by amido-groups, just like aurine, and affords a body resembling rosaniline, which must be considered as hexamethoxyl-rosaniline.

CARBOXYL DERIVATIVES OF THE TRIPHENYL METHANES. PHTHALIDES.

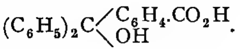
Of the many possible carboxyl derivatives of the triphenyl methanes (their amido- and phenol derivatives), there is one group of compounds of particular interest. These contain a carboxyl in the benzene nucleus in the ortho position (in relation to the combining methane carbon).*

By oxidation they yield carbinol acids, which, however (like all γ-oxyacids), are not stable, but immediately sustain a loss of water and pass into their anhydrides (lactones):—



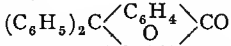
$$(C_6H_5)_2.C\begin{cases}C_6H_4.CO_2H\\H\end{cases}$$

Ortho-carboxylic Acid.



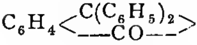
$$(C_6H_5)_2C\begin{cases}C_6H_4.CO_2H\\OH\end{cases}.$$

Carbinol-carboxylic Acid.



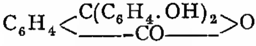
Anhydride.

These anhydrides bear exactly the same relation to the carbinol-carboxylic acids that the so-called *Phthalide* bears to the unstable ortho-oxy-methyl benzoic acid (p. 772). It is, therefore, convenient to regard the compounds belonging here as derivatives of phthalide, produced by the substitution of phenyls (oxy- and amidophenyls) for the hydrogen of the CH_2-group:—



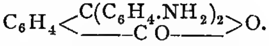
$$C_6H_4<\begin{matrix}C(C_6H_5)_2\\CO\end{matrix}>O$$

Diphenyl phthalide,
o-Phthalophenone.



$$C_6H_4<\begin{matrix}C(C_6H_4.OH)_2\\CO\end{matrix}>O$$

Dioxy-diphenylphthalide,
Dioxyphthalophenone.



$$C_6H_4<\begin{matrix}C(C_6H_4.NH_2)_2\\CO\end{matrix}>O.$$

Diamido-diphenyl phthalide,
Diamidophthalophenone.

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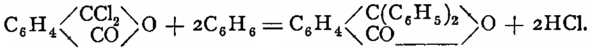
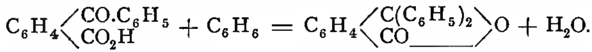
* See further, A. Baeyer, *Annalen*, 202, 36; 212, 347.

They are reduced to ortho-carboxylic acids, and may be obtained from phthalic acid in the same manner as phthalide, hence, their name. They are produced by the condensation of *o*-phthalyl chloride (or *o*-phthalic anhydride) with benzenes, by the action of $AlCl_3$:—



$$C_6H_4\left\langle\begin{matrix}CCl_2\\CO\end{matrix}\right\rangle O + 2C_6H_6 = C_6H_4\left\langle\begin{matrix}C(C_6H_5)_2\\CO\end{matrix}\right\rangle O + 2HCl.$$

In using phthalic anhydride, we first get *o*-benzoyl benzoic acid (p. 863). On permitting benzene and $AlCl_3$ to further act upon the latter, the product will be diphenylphthalide (*Berichte*, 14, 1865):—



$$C_6H_4\left\langle\begin{matrix}CO.C_6H_5\\CO_2H\end{matrix}\right. + C_6H_6 = C_6H_4\left\langle\begin{matrix}C(C_6H_5)_2\\CO\end{matrix}\right\rangle O + H_2O.$$

The diphenolphthalides (phthaleïns) are analogously produced by the condensation of phthalic anhydride with phenols (p. 881).

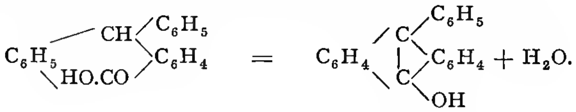
o-Benzoyl benzoic acid reacts similarly with phenols (on heating to 200°), and in this way phthalophenones can be obtained with one benzene and one phenol residue (*Berichte*, 14, 1859).

Diphenyl Phthalide, Phthalophenone, $C_{20}H_{14}O_2$, the anhydride of triphenyl carbinol-ortho-carboxylic acid, is obtained from phthalyl chloride with benzene and $AlCl_3$ (*Annalen*, **202**, 50), or with mercury diphenyl, and crystallizes from alcohol in leaflets, melting at 115°. When boiled with alkalies it dissolves to salts of triphenyl carbinol-ortho-carboxylic acid, which is again separated as anhydride (phthalophenone) by acids.

If the alkaline solution of the carbinol acid be boiled with zinc dust, we get **Triphenyl-methane-carboxylic Acid,** $(C_6H_5)_2CH.C_6H_4.CO_2H$, melting at 156°, and when carbon dioxide splits off it yields triphenyl methane. The same product is obtained from phenylphthalide (p. 863) and benzene with $AlCl_3$ (*Berichte*, **19**, Ref. 687).

Phthalophenone dissolves in nitric acid, yielding a dinitro product, whose diamido-derivative is converted by nitrous acid into dioxyphthalophenone (phenol phthaleïn) (*Annalen*, 202, 68).

An interesting reaction is that triphenyl-methane carboxylic acid can, by the elimination of water, yield phenylanthranol, a derivative of anthracene:—



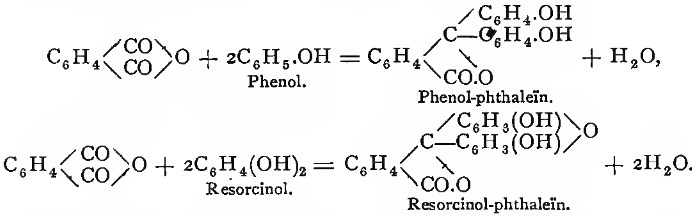
$$C_6H_5\left\langle\begin{matrix}CH\langle^{C_6H_5}\\HO.CO\end{matrix}\right\rangle C_6H_4 = C_6H_4\left\langle\begin{matrix}C\langle^{C_6H_5}\\ \vert\\ C\langle_{OH}\end{matrix}\right\rangle C_6H_4 + H_2O.$$

The derivatives of the acid deport themselves similarly (the so-called phthalins, p. 882); the resulting anthracene compounds are known as phthalidins (see these).

Oxyphthalophenone, $C_{20}H_{13}(OH)O_2$, Benzene-phenol-phthalide, can be obtained from phenol, in the same manner that phthalophenone is prepared from orthobenzoyl-benzoic acid with benzene. It melts at 155°. It forms the transition to the phthaleïns, containing two phenol residues. It dissolves in alkalies with a violet-red color, which disappears on heating, because the anhydride group is ruptured and the salt of the carbinol acid produced; this by reduction with zinc dust yields—

Oxy-triphenyl-methane Carboxylic Acid, $C_6H_5.CH\left\langle\begin{matrix}C_6H_4.OH\\C_6H_4.CO_2H\end{matrix}\right.$. This is a phthalin. Concentrated sulphuric acid abstracts water from it and converts it into its phthalidin (an anthracene derivative) (see above). Sulphuric acid decomposes oxyphthalophenone at 100° into phenol and *o*-benzoyl-benzoic acid. Fusion with potassium hydroxide converts it into benzoic acid and oxybenzophenone.

The **Phthaleïns**, the derivatives of phthalide containing two phenol residues, are particularly important, and are dyes which are of great technical value. A. v. Baeyer discovered them in 1871. They result from the condensation of phthalic anhydride (1 mol.) with phenols (2 mols.) on heating with sulphuric acid, or better, with $ZnCl_2$ to 120° (or with oxalic acid, p. 864):—

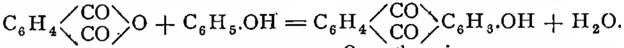


$$C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle O + \underset{\text{Phenol.}}{2C_6H_5.OH} = \underset{\text{Phenol-phthaleïn.}}{C_6H_4\left\langle\begin{matrix}C\left\langle\begin{matrix}C_6H_4.OH\\C_6H_4.OH\end{matrix}\right.\\CO.O\end{matrix}\right.} + H_2O,$$

$$C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle O + \underset{\text{Resorcinol.}}{2C_6H_4(OH)_2} = \underset{\text{Resorcinol-phthaleïn.}}{C_6H_4\left\langle\begin{matrix}C\left\langle\begin{matrix}C_6H_3(OH)\\C_6H_3(OH)\end{matrix}\right\rangle O\\CO.O\end{matrix}\right.} + 2H_2O.$$

The phthaleïns derived from di- and polyvalent phenols are all anhydrides, formed by the elimination of water from two phenol-hydroxyls (*Annalen*, **212**, 347).

The reaction proceeds as in the case of diphenylphthalide (p. 880); it may be assumed that oxybenzoyl-benzoic acid is first formed, and this then acts with a second molecule of the phenol. If, however, phthalic anhydride be heated to 150°, with but one molecule of phenol and sulphuric acid, anthraquinone derivatives are produced:—



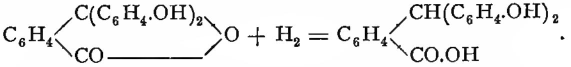
$$C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle O + C_6H_5.OH = C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle C_6H_3.OH + H_2O.$$

Oxyanthraquinone.

The free phthaleïns are generally colorless, crystalline bodies. They dissolve in the alkalies with intense colorations, and are again separated from their solutions by acids (even CO_2). The addition of concentrated caustic alkali causes the colors to disappear, because by the rupture of the anhydride group salts of the colorless carbinol acids are formed (p. 879). On diluting with water the colors reappear. The phthaleïns obtained from resorcinol and phthalic anhydride (or the anhydrides of polybasic fatty acids, p. 883) exhibit an intense fluorescence in these solutions, and are therefore termed *fluoresceïns*.

It appears the linking carbon atom (of phthalic acid) in them occupies the meta-position referred to the two hydroxyls of the resorcinol, and, therefore, only those meta-dioxybenzenes yield fluoresceïns in which the meta-position is unoccupied (*Berichte*, 15, 1375).

If the alkaline solutions of the phthaleïns be reduced with zinc dust, we obtain the non-coloring carboxylic acids (p. 879)—the *phthalins*:—



$$C_6H_4\left\langle\begin{matrix}C(C_6H_4.OH)_2\\CO\end{matrix}\right\rangle O + H_2 = C_6H_4\left\langle\begin{matrix}CH(C_6H_4.OH)_2\\CO.OH\end{matrix}\right. .$$

Phthaleïn. Phthalin.

The phthaleïns may be compared to the aurines, and the phthalins to the leucaurines (p. 876); in place of the hydroxyl of the latter the phthalins contain a carboxyl group. The hydroxyl, however, in the leucaurines is found in the para-position, while, in accordance with their method of production, the phthalins and phthaleïns contain the CO-group in the ortho position.

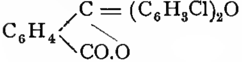
The phthalins dissolve in alkalies, oxidize, however, readily in alkaline solution (even in the air, more quickly by MnO_2 or MnO_4K), to phthaleïns. Another interesting reaction is the conversion of the phthalins, by mixing them with sulphuric acid, into the so-called *phthalidins* (p. 882), which by oxidation yield the phthalideïns (oxanthranol derivatives) (see Anthranol).

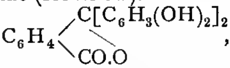
Phenol-phthaleïn, $C_{20}H_{14}O_4$, Dioxyphthalophenone, is also formed from phthalophenone when nitrous acid acts on the diamido-compound (p. 880). It is obtained on heating phthalic anhydride (3 parts) with phenol (4 parts) and tin chloride (4 parts), or with sulphuric acid to 115–120° for eight hours. The product is boiled with water, dissolved in sodium hydroxide and precipitated by acetic acid (*Annalen*, 202, 68). It is a yellow powder, crystallizing from alcohol in colorless crusts, and melting at 250°. It dissolves in the alkalies with a red color (see above). It is used as an indicator in alkalimetry, especially in determining carbon dioxide with baryta (*Berichte*, 17, 1077, 1097).

Acetic anhydride converts it into a diacetate, melting at 143°, and bromine into a tetrabromide, $C_{20}H_{10}Br_4O_4$. On fusion with alkalies it decomposes into benzoic acid and dioxybenzophenone (p. 860). Boiling with alkaline hydroxides and zinc dust changes phthaleïn into **Phenol-phthalin**, $C_{20}H_{16}O_4$, crystallizing from hot water in needles, and melting at 225°. It dissolves in alkalies without coloration; the solution oxidizes to phenol-phthaleïn in the air, more quickly with potassium ferricyanide or permanganate.

Resorcinol-phthaleïn, $C_{20}H_{12}O_5 + H_2O$, **Fluoresceïn**, is prepared by heating phthalic anhydride (5 parts) with resorcinol (7 parts) to 200°. When precipitated from its salts it is a yellowish-red powder, and when crystallized ($C_{20}H_{12}O_5$) from alcohol it is dark red in color. It decomposes about 290°. It dissolves in alcohol with a yellow-red color and green fluorescence. Its concentrated alkali solution is dark red, but on dilution it gradually becomes yellow, and then exhibits a magnificent yellowish-green fluorescence. When fused with caustic soda it decomposes into resorcinol and mono-resorcinol phthaleïn, which further splits up into phthalic acid (benzoic acid) and resorcinol. **Resorcinol-phthalin, Fluorescin**, $C_{20}H_{14}O_5$, formed by reduction with zinc dust, is a colorless, amorphous substance, which is again oxidized to fluoresceïn, when its alkaline solution is exposed to the air.

If bromine be allowed to act on fluoresceïn suspended in glacial acetic acid, we obtain substitution products, of which **Tetrabromfluoresceïn**, $C_{20}H_8Br_4O_5$, is the commercially important dye, **Eosin** (Caro). When thrown out of solution it is a yellowish-red precipitate; crystallized from alcohol it forms red crystals. The *potassium salt*, $C_{20}H_6K_2Br_4O_5$, containing 6 and 5 molecules of H_2O, is a red-brown powder with shining leaflets, and constitutes the eosin of commerce, soluble in water, and imparting to wool and silk a beautiful rose color (similar to cochineal). A benzyl derivative of fluoresceïn is the sodium salt of commercial *Chrysolin*, which dyes wool and silk directly, imparting to them a color resembling turmeric.

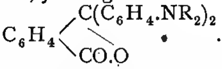
Phosphorus pentachloride converts fluoresceïn into **Fluoresceïn chloride**,  $C_6H_4\left\langle\begin{matrix}C = (C_6H_3Cl)_2O\\ \diagdown\\ CO.O\end{matrix}\right.$ (*Annalen*, 183, 18). Its halogen atoms are very reactive. It is used for the preparation of rhodamine (see below).

Pyrocatechin-phthaleïn, $C_{20}H_{14}O_6$ =  $C_6H_4\left\langle\begin{matrix}C[C_6H_3(OH)_2]_2\\ \diagdown\\ CO.O\end{matrix}\right.$, is produced when phthalic anhydride and pyrocatechin are heated to 140–150° with zinc chloride (*Berichte*, 22, 2197). It is a yellow, non-crystallizable mass. It dissolves in the caustic alkalies with a blue color, in the alkaline carbonates with a violet color. From its acid esters we would infer the presence of four hydroxyl groups in it; hence it does not form an inner anhydride.

Pyrogallol-phthaleïn, Galleïn, $C_{20}H_{10}O_7$ (see *Annalen*, 209, 249), is obtained on heating pyrogallic acid with phthalic anhydride to 200°. It dissolves with a dark red color in alcohol, and with a beautiful blue color in the alkalies. Zinc dust reduces it to *hydrogalleïn*, $C_{20}H_{12}O_7$, and then to *gallin*, $C_{20}H_{14}O_7$, which corresponds to phenol-phthalin.

Like all phthalins (p. 880), it is converted by sulphuric acid into the anthracene derivatives, *Coerulin*, $C_{20}H_{12}O_6$, and *Coeruleïn*, $C_{20}H_8O_6$. The latter dissolves in the alkalies with a green color, and finds application as a green dye.

Chlorinated phthalic acids can be substituted for phthalic acid in the preparation of the preceding compounds. Various fluoresceïns and eosins result. They acquire a violet-red color with the increasing number of halogen atoms (*Erythrosin*, *Phloxin*, etc).

Phthalic anhydride also reacts with dimethylaniline, yielding **Dimethylaniline-phthaleïn**, $C_{24}H_{24}N_2O_2$ =  $C_6H_4\left\langle\begin{matrix}C(C_6H_4.NR_2)_2\\ \diagdown\\ CO.O\end{matrix}\right.$. With phthalyl chloride we get an isomeric body, the so-called *Phthal-green*, which is probably a phthalidin, and is derived from anthracene (*Annalen*, 206, 92).

The phenols can combine with the anhydrides of dibasic fatty acids (oxalic, succinic, maleïc) and with tartaric acid, citric acid, etc. (*Berichte*, 15, 883, 18, 2864), yielding analogous phthaleïns and phthalins. **Succinyl fluoresceïn**, $C_{16}H_{12}O_5$, from succinic acid and resorcinol, yields a tetrabrom-derivative, $C_{16}H_8Br_4O_5$, very similar to *Eosin*.

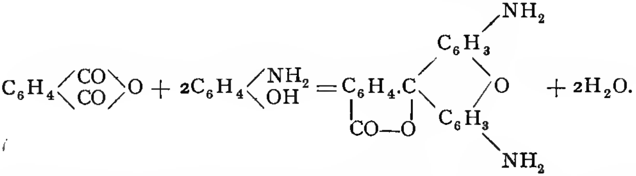
Rhodamines.

The *rhodamines*, the phthaleïns of *m* amido phenol, $C_6H_4(NH_2).OH$, and its derivatives, are of special importance. They are violet-red, magnificently fluorescent dyestuffs. In constitution they are perfectly analogous to the fluoresceïns; they contain two amido groups in place of the two hydroxyls:—

$C_{20}H_{10}O_3(OH)_2$
Fluoresceïn.

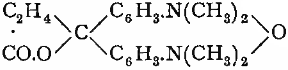
$C_{20}H_{10}O_3(NH_2)_2$
Rhodamine.

They correspond in all particulars to the rosamines (p. 877), and like them contain salt-forming groups of negative and positive nature. The *simplest* rhodamine is formed when *m*- amidophenol hydrochloride and phthalic anhydride are heated to 180–190° with sulphuric acid (*Berichte*, 21, Ref. 682):—



The hydrochloride salt forms metallic green leaflets. Its solutions are yellow in color and highly fluorescent. *The alkylic rhodamines* possess more intense colors. They are produced when the salt is heated with alkyl iodides. A better course to pursue in this preparation is the condensation of alkylic *m*- amido phenols (p. 681) and phenyl-*m*-amido phenol (*m*- oxydiphenylamine, p. 603) (*Berichte*, 21, Ref. 682, 920; 22, Ref. 788). Still another procedure consists in rearranging flouresceïn chloride (p. 883) by heating it with dialkylamines (*Berichte*, 22, Ref. 625, 789).

Succinic acid yields rhodamines.

Succino-rhodamine,  $\begin{array}{l}C_2H_4 \\ \cdot \\ CO.O\end{array}\!\!>C<\!\!\begin{array}{l}C_6H_3.N(CH_3)_2 \\ \\ C_6H_3.N(CH_3)_2\end{array}\!\!>O$, is apparently the commercial rhodamine S.

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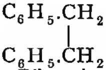
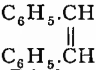
3. Derivatives with benzene nuclei joined by two or more carbon-atoms (p. 842).

THE DIBENZYL GROUP.



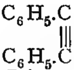
$\begin{array}{l}C_6H_5.CH_2 \\ \quad | \\ C_6H_5.CH_2\end{array}$

Dibenzyl.



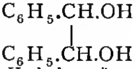
$\begin{array}{l}C_6H_5.CH \\ \quad \| \\ C_6H_5.CH\end{array}$

Toluylene.



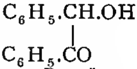
$\begin{array}{l}C_6H_5.C \\ \quad ||| \\ C_6H_5.C\end{array}$

Tolane.



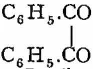
$\begin{array}{l}C_6H_5.CH.OH \\ \quad | \\ C_6H_5.CH.OH\end{array}$

Hydrobenzoïn.



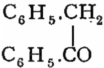
$\begin{array}{l}C_6H_5.CH.OH \\ \quad | \\ C_6H_5.CO\end{array}$

Benzoïn.



$\begin{array}{l}C_6H_5.CO \\ \quad | \\ C_6H_5.CO\end{array}$

Benzil.



$\begin{array}{l}C_6H_5.CH_2 \\ \quad | \\ C_6H_5.CO\end{array}$

Desoxybenzoïn.

Dibenzyl, $C_{14}H_{14}$ (symmetrical diphenyl ethane), is prepared by the action of sodium or (copper) upon benzyl chloride, $C_6H_5.CH_2Cl$, or of $AlCl_3$ upon benzene and ethylene chloride, and by heating stilbene and tolane, or benzoïn and desoxybenzoïn with hydriodic acid. It crystallizes in large prisms, melting at 52°, and boiling at 284°. It forms stilbene and toluene when heated to 500°. Chromic acid and potassium permanganate oxidize it directly to benzoic acid.

It yields two dinitro-compounds by nitration.

pp-**Dinitrodibenzyl**, $NO_2.C_6H_4.CH_2.CH_2.C_6H_4.NO_2$, has also been obtained by the action of stannous chloride upon *p*-nitrobenzyl chloride, $NO_2.C_6H_4.CH_2Cl$. It crystallizes in yellow needles and melts at 179° (*Annalen*, 238, 272). **Diamidodibenzyl**, $H_2N.C_6H_4.C_2H_4.C_6H_4.NH_2$, and its tetramethyl derivative are, in distinction to the corresponding diphenylmethane derivatives, bases that lack coloring power (*Berichte*, 20, 914).

Stilbene, Toluylene, $C_{14}H_{12} = C_6H_5.CH{:}CH.C_6H_5$, symmetrical diphenyl ethylene, is produced in various ways, thus: by distilling benzyl sulphide and disulphide; by the action of sodium upon bitter-almond oil or benzal chloride, $C_6H_5.CHCl_2$; by conducting dibenzyl or toluene vapors over heated lead oxide; by heating diphenyl monochlorethane alone or diphenyl trichlorethane with zinc dust, by reducing tolane with zinc dust and glacial acetic acid, or sodium and alcohol. An interesting method for its production is that of distilling fumaric and cinnamic phenyl esters (*Berichte*, 18, 1945). It crystallizes in large monoclinic leaflets or prisms, dissolves easily in hot alcohol, melts at 120°, and distils at 306°.

When heated with hydriodic acid it yields dibenzyl, $C_{14}H_{14}$. Chromic acid oxidizes it to bitter-almond oil and benzoic acid. It is immediately attacked by potassium permanganate, while phenanthrene does not react.

Bromine combines with stilbene, forming **Stilbene Dibromide**, $C_6H_5.CHBr.CHBr.C_6H_5$, dibromdibenzyl. It is also prepared from dibenzyl by the action of bromine and from the two hydrobenzoïns by means of PBr_5. It consists of silky needles, melting at 237°. Alcoholic potassium hydroxide converts it into **bromstilbene**, $(C_6H_5)_2C_2HBr$ (melting at 25°), and then into tolane.

With chlorine, stilbene (in chloroform solution) yields *α*-**Stilbene Chloride**, $(C_6H_5)_2C_2H_2Cl_2$, which is also obtained from hydro- and isohydrobenzoïn with PCl_5. It melts at 192°. *β*-**Stilbene Chloride** is produced at the same time from hydrobenzoïn. It melts at 93°, and after heating to 200°, yields the *α*-compound on crystallizing (*Annalen*, 198, 131).

The action of alcoholic potash upon *o*-nitrobenzyl chloride (p. 584) gives rise to two alloisomeric *o*-**Dinitro-stilbenes**, $(C_6H_4.NO_2)_2.C_2H_2$, melting at 126° and 127°. The first is the maleïnoid or *cis* variety, while the second represents the *trans*-form (*Berichte*, 21, 2071; 23, 2073). *p*-Nitrobenzyl chloride also yields two alloisomeric *p-Dinitro-stilbenes* (*Berichte*, 23, 1938). The principal portion of the product melts at 250° (280°), and upon reduction yields *pp*-**Diamidostilbene**, $H_2N.C_6H_4.C_2H_2.C_6H_4.NH_2$, melting at 227°. It can also be obtained from *p*-nitrotoluene by the action of caustic soda and further reduction with stannous chloride (*Berichte*, 19, 3238). It combines similarly to benzidine with the naphthol sulphonic acids, forming substantive blue azo-dyes (*Berichte*, 22, Ref. 311).

Tolane, $C_{14}H_{10} = C_6H_5.C \equiv C.C_6H_5$, Diphenyl Acetylene, is produced from stilbene bromide on boiling with alcoholic potash. It is easily soluble in alcohol and ether, and consists of large crystals, melting at 60°. Chromic acid oxidizes it to benzoic acid.

Two tolane dichlorides, $C_{14}H_{10}Cl_2$, result on conducting chlorine into tolane (in chloroform solution). They can also be prepared by reducing tolane tetrachloride with iron and acetic acid (*Berichte*, 17, 1165, 833); the α- melts at 143°, the β- at 63°. The first is supposed to be the plane symmetrical, maleïnoid form, the second the fumaroid form (*Annalen*, **248**, 18). Tolane also yields two dibromides, $C_{14}H_{10}Br_2$, with bromine, the α-variety melting at 208°, the β- at 64°. Both regenerate tolane on treatment with alcoholic potash.

Tolane Tetrachloride, $C_{14}H_{10}Cl_4$, is produced from chlorobenzil (p. 889) with PCl_5, by chlorinating toluene (together with $C_6H_5.CCl_3$) and by heating $C_6H_5.CCl_3$ with copper. It consists of brilliant crystals, which become porcelanous at 100° and melt at 163°. Heated with sulphuric acid to 165°, or glacial acetic acid to 200°, it yields benzil.

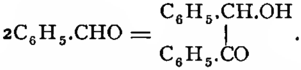
Hydrobenzoïns, $C_{14}H_{14}O_2 = C_6H_5.CH(OH).CH(OH).C_6H_5$. Toluylene Glycols. Two isomeric bodies—hydrobenzoïn and isohydrobenzoïn—are produced when zinc and alcoholic hydrochloric acid act upon oil of almonds, or when the latter is treated with sodium amalgam. Both are also obtained from stilbene bromide or chloride, on converting the latter by silver acetate or benzoate into esters, and saponifying these with alcoholic ammonia. With potassium acetate, isohydrobenzoïn is almost the sole product. Hydrobenzoïn predominates (with a little isohydrobenzoïn) when sodium amalgam acts on benzoïn. This is also the best method for its preparation (*Annalen*, **248**, 36).

PBr_5 converts both into the same stilbene bromide (melting at 237°); and with PCl_5 both yield α-stilbene chloride (the β-chloride is also produced from hydrobenzoïn). Chromic acid oxidizes both to bitter-almond oil and benzoic acid, but with nitric acid benzoïn and benzil are the products. All these reactions prove that the two hydrobenzoïns possess the same structural formula (see *Annalen*, **198**, 191), and that relations analogous to those observed with the dialkyl succinic acids, the tolane chlorides, etc., are also present here. Stereochemically considered hydrobenzoïn is the fumaroïd, and isohydrobenzoïn the malenoïd form (*Annalen*, **258**, 186).

Hydrobenzoïn dissolves with difficulty in water, is readily soluble in alcohol, crystallizes in large, shining, rhombic plates, melting at 134° and sublimes without decomposition. The *diacetate*, $C_{14}H_{12}(O.C_2H_3O)_2$, is obtained from benzaldehyde and acetyl chloride by means of zinc dust; it consists of large prisms, melting at 134°. Diphenyl aldehyde (p. 861) and hydrobenzoïn-anhydride, $(C_6H_5)_2C_2H_2O$, melting at 132° (see *Annalen*, **258**, 186), are produced when hydrobenzoïn is boiled with sulphuric acid (20%).

Isohydrobenzoïn is more easily soluble in water than the preceding isomeride. It crystallizes in shining, four-sided prisms which contain water of crystallization, and rapidly effloresce on exposure. It crystallizes from alcohol in an anhydrous form, and melts at 119.5°. Its *diacetate* is dimorphous, and crystallizes in shining leaflets, melting at 118°, or in rhombic prisms melting at 106°. Isohydrobenzoïn, boiled with sulphuric acid, yields its *anhydride*, $(C_6H_5)_2C_2H_2O$, melting at 102° (together with a little diphenyl aldehyde).

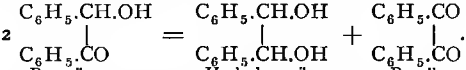
Benzoïn, $C_{14}H_{12}O_2 = C_6H_5.CH(OH).CO.C_6H_5$, a ketone alcohol, is produced when hydro- and isohydrobenzoïn are oxidized with concentrated nitric acid, and by the action of potassium cyanide upon benzaldehyde in alcoholic solution (*Berichte*, **21**, 1296):—



$$2C_6H_5.CHO = \begin{array}{l} C_6H_5.CH.OH \\ \quad | \\ C_6H_5.CO \end{array} .$$

All aromatic aldehydes afford the latter reaction; this is also true of furfurol (p. 524). It is analogous to the condensation of the ketones to pinacones (p. 202) and to the conversion of aldehydes into alcohols and acids by alcoholic potash. The products are termed *benzoïns*, and are capable of reducing Fehling's solution, even at ordinary temperatures, when they are oxidized to benzils (diketones).

Benzoïn dissolves with difficulty in water, cold alcohol and ether; it crystallizes in shining prisms, and melts at 134°. Nascent hydrogen converts it into hydrobenzoïn. When its alcoholic solution is digested with phenylhydrazine it forms the *hydrazone*, $C_{14}H_{12}O(N_2H.C_6H_5)$, melting at 155°. When oxidized with chromic acid, it breaks up into benzaldehyde and benzoic acid. Hydrobenzoïn and benzil (along with benzilic acid) are produced on boiling with alcoholic potash:—

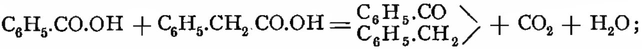


$$2\begin{array}{l} C_6H_5.CH.OH \\ \quad | \\ C_6H_5.CO \end{array} = \begin{array}{l} C_6H_5.CH.OH \\ \quad | \\ C_6H_5.CH.OH \end{array} + \begin{array}{l} C_6H_5.CO \\ \quad | \\ C_6H_5.CO \end{array} .$$

Benzoïn. Hydrobenzoïn. Benzil.

Anisoïn, from anisic aldehyde, and *cuminoïn*, from cumin aldehyde, are very similar to benzoïn, and yield perfectly analogous derivatives (desoxybenzoïns, benzils and benzilic acids) (*Berichte*, 14, 323). $CSCl_2$ converts the benzoïns into beautifully colored compounds, called *desaurines* (*Berichte*, 21, 2445).

Desoxybenzoïn, $C_{14}H_{12}O = C_6H_5.CO.CH_2.C_6H_5$, *phenyl-benzyl ketone*, is obtained by reducing benzoïn or chlorobenzil, $C_6H_5.CO.CCl_2.C_6H_5$, with zinc and hydrochloric acid; by heating monobromtoluylene with water to 180–190°; by distilling a mixture of calcium benzoate and calcium phenyl-acetate:—



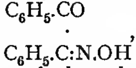
$$C_6H_5.CO.OH + C_6H_5.CH_2.CO.OH = \left.\begin{array}{l} C_6H_5.CO \\ C_6H_5.CH_2 \end{array}\right> + CO_2 + H_2O;$$

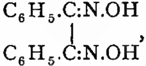
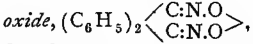
further, when $AlCl_3$ acts upon a mixture of alphatoluic chloride, $C_6H_5.CH_2.CO.Cl$ and benzene (*Berichte*, 19, 1064); and most easily by the reduction of benzoïn with zinc and hydrochloric acid (*Berichte*, 21, 1296).

Phenyl-benzyl ketone crystallizes from alcohol in large plates, melting at 60° and boiling at 314°. One H-atom of its CH_2-group can be replaced by sodium and alkyls, but not the second (*Berichte*, 21, 1297; 23, 2071). Nitrous acid, or amyl nitrite, converts it into *isonitroso*-desoxybenzoin, melting at 135°, and identical with benzil monoxime (see below). It forms an *oxime*, melting at 98°, with hydroxylamine. Bromine converts desoxybenzoïn into *Desylbromide*, $(C_6H_5)_2C_2HBrO$, melting at 55° (*Berichte*, 21, 1355). It yields dibenzyl when heated with hydriodic acid. Sodium amalgam converts it into *toluylene hydrate*, $C_{14}H_{14}O = C_6H_5.CH(OH).CH_2.C_6H_5$, melting at 62°. Nitric acid again oxidizes it to desoxybenzoïn. See *Berichte*, 22, 1229, for methyl desoxybenzoïns.

Benzil, $C_{14}H_{10}O_2 = C_6H_5.CO.CO.C_6H_5$, *Dibenzoyl*, an *a*-diketone, is produced in the oxidation of benzoïn with chlorine; and by heating toluylene bromide with water and silver oxide (together with toluylene). It crystallizes from ether in large, six-sided prisms, melting at 90° and boiling at 347°.

Benzil-dihydrazone, $(C_6H_5)_2C_2(N_2H.C_6H_5)_2$, is produced on digesting phenylhydrazine hydrochloride and benzil. It melts at 225° (*Annalen*, 232, 230). It forms triphenyl-osotriazone when heated to 210° (p. 553). An isomeric dihydrazone has not been prepared (*Berichte*, 21, 2806).

One molecule of hydroxylamine, acting upon benzil, produces two alloisomeric **benzil-monoximes**,  $\begin{array}{l}C_6H_5.CO\\ \quad\quad\cdot\\ C_6H_5.C:N.OH\end{array}$, the *a*- melting at 138°, and the *γ*- at 114°. The former passes into the latter by heating it to 100° with alcohol, or upon dissolving it in glacial acetic acid with hydrochloric acid. *a*-Monoxime and hydroxylamine form *a*-benzil dioxime, while the *γ*-monoxime yields *γ*-benzil dioxime. The expected *β*-benzil monoxime has not been discovered (*Berichte*, 22, 540, 709). See *Berichte*, 22, 1998, for the benzyl ethers of the benzil monoximes.

Two molecules of hydroxylamine convert benzil into two alloisomeric **benzil dioximes**,  $\begin{array}{l}C_6H_5.C:N.OH\\ \quad\quad\;|\\ C_6H_5.C:N.OH\end{array}$, the *a*- melting at 237°, and the *β*- at 207°. A third *γ*-benzil dioxime has been prepared from *β*-benzil monoxime and hydroxylamine (see above); it melts below 100°, loses its water of crystallization, and then remelts at 164–166°, passing at the same time into the *β*-dioxime (*Berichte*, 22, 709). When the three dioximes are heated to 100° with hydrochloric acid, they are resolved into $2NH_2.OH$ and benzil. They yield three different diacidyl esters with acid anhydrides. By elimination of water they all form the same *anhydride*, $(C_6H_5)_2C_2N_2O$, melting at 94°. Potassium ferricyanide, in alkaline solution, oxidizes all three to the same *oxide*,  $(C_6H_5)_2\left\langle\begin{array}{l}C:N.O\\C:N.O\end{array}\right\rangle$, melting at 114°; when rapidly distilled, it becomes phenyl-cyanate. Carbanilido-derivatives are produced by the union of the three benzil dioximes with phenyl-cyanate (*Berichte*, 22, 3111). Glacial acetic acid and hydrochloric acid acting upon *β*-benzil dioxime rearranges it to oxanilide, $C_6H_5.NH.CO.CO.NH.C_6H_5$ (see benzophenoxime, p. 858), whereas *a*-benzil dioxime yields dibenzenyl azoxime (p. 718) (*Berichte*, 22, Ref. 592).

Far-reaching theories, based on van't Hoff's ideas have been proposed to explain the differences in the three structurally identical benzil dioximes (*Berichte*, 21, 946, 3510; 22, 705); but they have proved insufficient (*Berichte*, 23, 2405). At the present writing the inclination is to refer the isomerism to the nitrogen atom of the hydroxylamine (p. 719). It has been attempted to construct theories of great import upon very few facts.* Chromic acid oxidizes it to benzoic acid.

When benzil is allowed to stand for some time, with alcohols and some potassium cyanide, it sustains a decomposition into benzoic ester and benzaldehyde, which further changes to benzoic acid. Furil, but not isatin, reacts similarly.

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* "Hypotheses non fingo."—*Newton*,

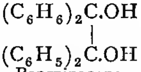
When digested with PCl_5 benzil yields **chlorobenzil**, $C_6H_5.CO.CCl_2.C_6H_5$, melting at 61°. Benzil, when heated with alcoholic potash, is converted into benzilic acid (p. 862). In this case a molecular rearrangement takes place similar to that observed with the pinacones.

Isobenzil, $C_{14}H_{10}O_2$, is isomeric with the preceding, and is obtained from benzoyl chloride, $C_6H_5.CO.Cl$, in alcoholic solution, by means of sodium amalgam. It forms, in distinction to benzil, *white* needles, melting at 156° and boiling at 314°. It forms β-benzil dioxime with hydroxylamine (*Berichte*, 21, 808).

Anisil, $(CH_3.O.C_6H_4)_2C_2O_2$, from *anisoïn* and *cuminil*, $(C_3H_7.C_6H_4)_2C_2O_2$, from *cuminoïn* (above), behave like benzil. When they are boiled or fused with caustic potash, they afford *anisilic acid*, $(CH_3.O.C_6H_4)_2C(OH).CO_2H$, and *cuminilic acid*, $(C_3H_7.C_6H_4)_2C(OH).CO_2H$. Anisil forms two dioximes with hydroxylamine (*Berichte*, 22, 372).

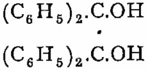
Pinacones and Pinacolines.

Nascent hydrogen, acting on the benzo-ketones, converts them, through a condensation of two molecules, into the *pinacones* (together with slight quantities of the secondary alcohols), which are also bivalent alcohols (glycols). In this behavior they resemble the ketones of the fatty series (p. 202). From benzophenone we get benzhydrol (p. 857) and benzpinacone:—



$$\underset{\text{Benzophenone.}}{(C_6H_5)_2CO} \text{ yields } \underset{\text{Benzhydrol.}}{(C_6H_5)_2CH.OH} \text{ and } \underset{\text{Benzpinacone.}}{\begin{array}{c}(C_6H_6)_2C.OH\\ |\\ (C_6H_5)_2C.OH\end{array}}.$$

These pinacones, just like those of the fatty series, readily part with water (by heating with sulphuric or hydrochloric acid, or by the action of all reagents, which otherwise act upon hydroxyl—acetyl chloride, hydriodic acid and PCl_5) and by an atomic rearrangement become *pinacoline ketones*:—



$$\begin{array}{c}(C_6H_5)_2.C.OH\\ \cdot\\ (C_6H_5)_2.C.OH\end{array} \text{ yields } \underset{\text{Benzpinacoline.}}{(C_6H_5)_3C.CO.C_6H_5} + H_2O.$$

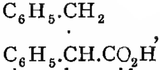
An analogous change occurs in the conversion of benzil into benzilic acid (see above), and of phenanthraquinone into diphenylene glycollic acid (p. 851). Therefore, the conception of the pinacone bodies may be further extended to all alcohols having two adjacent OH-groups (comp. *Annalen*, 198, 144).

Benzpinacone, $C_{26}H_{22}O_2$, formed from benzophenone by the action of zinc and sulphuric acid (*Berichte*, 14, 1402), crystallizes from alcohol in shining, small prisms, melting at 185° and splitting into benzophenone and benzhydrol. It sustains a like change when boiled with alcoholic potash.

On heating benzpinacone with hydrochloric or dilute sulphuric acid to 200°, by the action of methyl chloride upon it, or of zinc dust and acetyl chloride upon benzophenone, we get two

Benzpinacolines, $C_{26}H_{20}O$—the α-, melting at 205°, the β-variety, at 179° (*Berichte*, 17, 912). Both decompose into triphenyl methane, $(C_6H_5)_3CH$, and benzoic acid, on boiling with alcoholic potash.

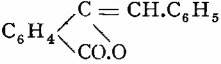
Carboxyl Derivatives.



Dibenzyl Carboxylic Acid, $\begin{array}{c}C_6H_5.CH_2\\ \cdot\\ C_6H_5.CH.CO_2H\end{array}$, Benzylphenyl Acetic Acid, results upon introducing benzyl into benzyl cyanide, etc. It melts at 91°, and boils about 335° (*Berichte*, 21, 1315).

Diphenyl Acrylic Acid, *a*-Phenyl Cinnamic Acid, $C_6H_5.CH:C(C_6H_5).CO_2H$, formed by the condensation of phenyl-acetic acid, $C_6H_5.CH_2.CO_2H$, with benzaldehyde, melts at 170°. Sodium amalgam converts it into dibenzyl carboxylic acid.

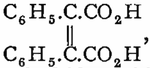
o-**Benzil Carboxylic Acid**, $C_6H_5.CO.CO.C_6H_4.CO_2H$, exists in two alloisomeric forms, resulting from the oxidation of desoxybenzoïn carboxylic acid. The *yellow* colored modification melts at 141°, the *white* at 125–130°. Both afford the same ethyl ester, and the same monoxime (melting at 160°) (*Berichte*, 23, 1344, 2079).

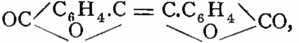
o-**Desoxybenzoïn Carboxylic Acid**, $C_6H_5.CH_2.CO.C_6H_4.CO_2H$, may be obtained by boiling benzylidene phthalide with alkalies. It crystallizes with one molecule of water, and melts at 75°. The corresponding lactone, **Benzylidene Phthalide**,  $C_6H_4\left\langle\begin{matrix}C = CH.C_6H_5\\ \diagdown\\ CO.O\end{matrix}\right.$ (see p. 352), results from the condensation of phthalic anhydride with phenyl-acetic acid (*Berichte*, 18, 3470). It melts at 99°. It forms salts of desoxybenzoïn carboxylic acid when boiled with alkalies.

Dicarboxylic Acids.

Diphenyl-succinic Acid, $C_{16}H_{14}O_4$, Dibenzyl-dicarboxylic Acid, occurs, similarly to the dialkyl succinic acids (p. 419) and hydrobenzoïn, in two alloisomeric forms. The *a-acid* is produced on heating phenyl-bromacetic acid with alcoholic CNK (*Berichte*, 23, 117), also (together with the *β*-acid), from the anhydride of stilbene dicarboxylic acid (*Berichte*, 14, 1802; *Annalen*, 259, 61). Its dinitrile, $(C_6H_5)_2C_2H_2(CN)_2$, is obtained from phenyl-brom-acetonitrile with potassium cyanide. The acid crystallizes from water in prisms, containing one molecule of water, melts at 185° when rapidly heated, loses water and remelts at 220°. When heated to 200° with hydrochloric acid it changes to the *β*-acid. Its *anhydride*, melting at 116°, is readily produced by means of acetyl chloride.

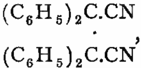
The isomeric *β*-**Dibenzyl-dicarboxylic Acid** is produced from the anhydride of stilbene dicarboxylic acid with sodium amalgam; and from dicyan stilbene, $(C_6H_5)_2C_2(CN)_2$, when heated with sodium amalgam or when heated with hydrochloric acid. It is insoluble in water and melts at 229°, when it yields water and the anhydride of the *a*-acid. It also yields the *anhydride* (but with more difficulty) when heated with acetyl chloride (*Berichte*, 23, Ref. 574, 646). It melts at 112°.

Stilbene Dicarboxylic Acid, $C_{16}H_{12}O_4$ =  $\begin{matrix}C_6H_5.C.CO_2H\\ \|\\ C_6H_5.C.CO_2H\end{matrix}$, if separated from its salts, at once decomposes into water and its anhydride, melting at 155°. The *nitrile*, $(C_6H_5)_2C_2(CN)_2$, dicyanstilbene, is derived from phenyl-brom-acetic nitrile, $C_6H_5.CHBr.CN$ (*Berichte*, 14, 1797), with alcoholic potassium cyanide. It melts at 158°. It passes into salts of stilbene dicarboxylic acid when boiled with alkalies.

Diphthalyl Acid, $HCO_2.C_6H_4.CO.CO.C_6H_4.CO_2H$, *oo*-**Benzil-dicarboxylic Acid**, from diphthalyl by oxidation, or by the action of zinc dust and acetic acid upon phthalic anhydride and further oxidation (*Berichte*, 21, Ref. 7) is only known in a single *white* modification (see benzylic acid), melting at 270°. It however, yields two series of dialkyl esters, white and yellow colored (*Berichte*, 23, 1347, 2080). It forms the anhydride, $C_{16}H_8O_5$, when heated to 200° with acetic anhydride; it melts at 165°. When heated with hydriodic acid it is reduced to **Diphthalyl**,  $OC\left\langle\begin{matrix}C_6H_4.C\\ O\end{matrix}\right. = \left.\begin{matrix}C.C_6H_4\\ O\end{matrix}\right\rangle CO$, which may be obtained by the condensation of phthalic anhydride with phthalide (p. 772), aided by sodium acetate. It melts at 334° (*Berichte*, 19, Ref. 695).

Tetraphenyl Ethane, $C_{26}H_{22} = (C_6H_5)_2CH.CH(C_6H_5)_2$, is obtained from benzophenone by heating with zinc dust (along with diphenyl methane and tetraphenyl-ethylene); from benzpinacone and benzpinacoline with hydriodic acid and phosphorus; from benzhydrol chloride, $(C_6H_5)_2CHCl$, by the action of zinc; from tetraphenyl ethylene by sodium and alcohol, and from tetrabromethane or stilbene bromide by means of benzene and $AlCl_3$ (*Berichte*, 18, 657). It crystallizes from acetic acid or benzene in large prisms, melting at 209°.

Tetraphenyl Ethylene, $C_{26}H_{20} = (C_6H_5)_2C:C(C_6H_5)_2$, formed together with tetraphenyl ethane, from benzophenone, is also obtained on heating benzophenone chloride, $(C_6H_5)_2CCl_2$, with silver. It crystallizes from benzene in fine needles, melting at 221°. Both hydrocarbons are split into two molecules of benzophenone when oxidized.

Tetraphenyl Ethylene Cyanide, 

$$\begin{matrix}(C_6H_5)_2C.CN\\ \cdot\\ (C_6H_5)_2C.CN\end{matrix}$$

, is obtained from diphenylacetic nitrile (p. 861) by means of metallic sodium and iodine (*Berichte*, 22, 1227). Its acid, **tetraphenyl-succinic acid**, $(C_6H_5)_4C_2(CO_2H)_2$, has been obtained from diphenyl chloracetic ester and melts at 261°.

Derivatives, containing benzene nuclei linked by a chain of three or four carbon atoms, are:—

Dibenzyl Ketone, $(C_6H_5.CH_2)_2CO$, produced on distilling calcium alphatoluate; it melts at 30° and boils at 320°. It forms an *oxime* with hydroxylamine, melting at 119°. One hydrogen atom of each of the two CH_2-groups can be replaced by alkyls (*Berichte*, 21, 1317). When reduced with hydriodic acid it forms **Dibenzyl methane**, $(C_6H_5.CH_2)_2CH_2$, boiling at 290–300°.

Dibenzoyl Methane, $(C_6H_5\ CO)_2CH_2$, is formed upon boiling dibenzoyl acetic acid with water. It crystallizes in large plates, melting at 81°, and distilling without decomposition (*Berichte*, 20, 655). The rearrangement of its isonitroso derivative, $(C_6H_5.CO)_2C:N.OH$, or its bromide, results in the production of

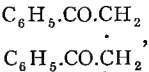
Diphenyl Triketone, $C_6H_5.CO.CO.CO.C_6H_5$. A brown oil, boiling at 289° (175 mm. pressure). It solidifies to a golden yellow mass, melting at 70°. In the air it combines with water to a colorless hydrate (*Berichte*, 23, 3378).

Tribenzoyl Methane, $(C_6H_5.CO)_3CH$, obtained from dibenzoyl methane and benzoyl chloride with sodium ethylate, melts at 225°. It does not possess acid properties (see dibenzoyl acetone (p. 731) (*Berichte*, 21, 1153).

Dibenzyl Acetic Acid, $(C_6H_5.CH_2)_2.CH.CO_2H$, is derived from dibenzoylmalonic acid. It melts at 87°, and is insoluble in water. Its *nitrile* melts at 90°; its CH-group cannot be substituted (*Berichte*, 2, 1328).

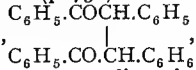
Dibenzyl Glycollic Acid, $C_{16}H_{16}O_3 = (C_6H_6.CH_2)_2C(OH).CO_2H$, **Oxatolylic Acid**, is produced from dibenzyl ketone by means of CNK and hydrochloric acid, and when vulpic and pulvic acids are boiled with dilute alkalies. It is almost insoluble in water, and crystallizes from alcohol in prisms, melting at 156°. When boiled with concentrated potassium hydroxide it decomposes into oxalic acid and two molecules of toluene (*Annalen*, 219, 41).

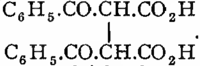
Dibenzoyl Acetic Acid, $(C_6H_5.CO)_2CH.CO_2H$ (p. 765), breaks down into dibenzoyl methane.

Diphenacyl, 

$$\begin{matrix}C_6H_5.CO.CH_2\\ \cdot\\ C_6H_5.CO.CH_2\end{matrix}$$

, **Dibenzoyl Ethane**, is produced by the decomposition of phenacyl-benzoyl acetic ester (p. 765). It consists of needles, melting at 145° (*Berichte*, 21, 3056). Being a γ-diketone it can eliminate water and yield diphenylfurfurane, and with P_2S_5 form diphenylthiophene, and with ammonia diphenylpyrrol (p. 731).

Bidesyl,  $\begin{array}{l} C_6H_5.COCH.C_6H_5 \\ \qquad\quad | \\ C_6H_5.CO.CH.C_6H_6 \end{array}$, dibenzoyl-diphenyl ethane, results when desylbromide acts upon sodium desoxybenzoïn (p. 887). It crystallizes from hot benzene, in needles, melting at 255°. *Isobidesyl,* formed simultaneously, melts at 161° (*Berichte,* 21, 1355). Bidesyl is identical with hydro-oxy-lepidene. Bidesyl and isobidesyl, being γ-diketones, form tetraphenyl pyrrol (p. 543) when heated with ammonia. Concentrated hydrochloric acid converts them into tetraphenyl furfurane, $C_4(C_6H_5)_4O$ (p. 524) with *lepidene* (*Berichte,* 22, 855, 2880).

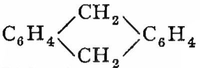
Dibenzoyl Succinic Acid, $C_{18}H_{14}O_6$ =  $\begin{array}{l} C_6H_5.CO.CH.CO_2H \\ \qquad\qquad\quad | \\ C_6H_5.CO.CH.CO_2H \end{array}$. Its diethyl ester is obtained from sodium benzoyl acetic ester (p. 763) by the action of iodine, just as we form di-aceto-succinic ester from aceto-acetic ester. On boiling the ester with dilute sulphuric acid we get (by saponification and elimination of water) its anhydride the *mono-lactone* $C_{16}H_{12}O_5$ (corresponding to carbopyrotritartaric acid), which very probably represents diphenyl-furfurane dicarboxylic ester.

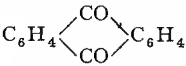
Vulpic Acid, $C_{19}H_{14}O_5$, is intimately related to dibenzyl acetic acid, and occurs in the lichen *Cetraria vulpina* and in a certain moss (12 per cent.), from which it may be extracted by chloroform or lime water. It is sparingly soluble in water and ether, crystallizes from alcohol in yellow prisms, melting at 110° and subliming. When boiled with lime water it is converted into methyl alcohol and *pulvic acid,* $C_{18}H_{12}O_5$. The latter melts at 214°, and when boiled with alkalies yields $2CO_2$ and dibenzyl glycollic acid. When boiled with ammonia and zinc dust it forms **Hydrocornicularic Acid,** $C_{17}H_{16}O_3$. This breaks down into toluene and phenyl succinic acid when heated with caustic potash (*Berichte,* 14, 1686).

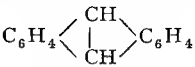
Diphenacyl Malonic Ester, $(C_6H_5.CO.CH_2)C(CO_2R)_2$, is produced by the interaction of acetophenone bromide and sodmalonic ester. The free acid loses carbon dioxide and forms **Diphenacyl Acetic Acid,** $(C_6H_5.CO.CH_2)_2CH.CO_2H$, which by the action of ammonia and the production of a closed ring by the group $CO.CH_2.CHR.CH_2.CO$, yields diphenyl *pyridine* carboxylic acid.

ANTHRACENE GROUP.

The members of this group contain two benzene nuclei, joined to each other by two doubly united carbon-atoms. In each benzene nucleus two ortho-positions are occupied. Therefore, we may designate them *Diortho-diphenylene Derivatives* (p. 850); usually, however, their names are derived from anthracene, from which they were first obtained :—

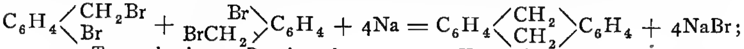

Diphenylene Dimethylene Hydranthracene.


Diphenylene Diketone Anthraquinone.


Anthracene.

Hydranthracene passes readily into anthracene by the loss of two hydrogen atoms; whereby we may suppose a mutual union of the two methane carbons takes place. Therefore, anthracene is mostly formed by its synthetic methods. Of the numerous syntheses of anthracene and diphenylene derivatives, analogous to those of the diphenyl methane derivatives (comp. p. 852), only such will be noticed, as are necessary for the establishment of the constitution of the compounds.

Hydranthracene is obtained from ortho-brom-benzyl bromide, $C_6H_4Br.CH_2Br$, by the action of sodium upon the ethereal solution; the bromine atoms of two molecules are withdrawn, and the residues combine (*Berichte*, 12, 1965):—

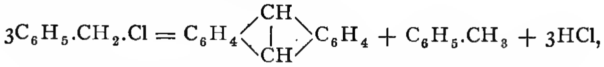


$$C_6H_4\left\langle\begin{matrix}CH_2Br\\Br\end{matrix}\right. + \left.\begin{matrix}Br\\BrCH_2\end{matrix}\right\rangle C_6H_4 + 4Na = C_6H_4\left\langle\begin{matrix}CH_2\\CH_2\end{matrix}\right\rangle C_6H_4 + 4NaBr;$$

Two molecules. α-Brombenzyl-bromide. Hydranthracene.

at the same time two hydrogen-atoms separate from the hydranthracene and large quantities of anthracene are produced.

Anthracene is likewise obtained (together with toluene) from benzyl chloride, on heating it with aluminium chloride:—



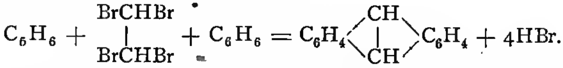
$$3C_6H_5.CH_2.Cl = C_6H_4\left\langle\begin{matrix}CH\\|\\CH\end{matrix}\right\rangle C_6H_4 + C_6H_5.CH_3 + 3HCl,$$

or with water to 200°, when dibenzyl will also be produced:—

$$4C_6H_5.CH_2Cl = C_{14}H_{10} + (C_6H_5.CH_2)_2 + 4HCl.$$

Anthracene (together with diphenyl methane) results also from the action of $AlCl_3$ upon benzene and CH_2Cl_2 (2 molecules).

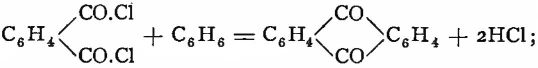
A noteworthy synthetic method is that from benzene and symmetrical tetrabrom-methane with $AlCl_3$ (*Berichte*, 16, 623):—



$$C_6H_6 + \begin{matrix}BrCHBr\\|\\BrCHBr\end{matrix} + C_6H_6 = C_6H_4\left\langle\begin{matrix}CH\\|\\CH\end{matrix}\right\rangle C_6H_4 + 4HBr.$$

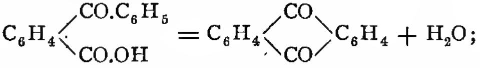
Dimethylanthracene hydride, $C_6H_4\left\langle\begin{matrix}CH(CH_3)\\CH(CH_3)\end{matrix}\right\rangle C_6H_4$, is similarly formed from benzene and ethidene chloride or bromide.

The formation of anthraquinone or diphenylene diketone from phthalic chloride and benzene, by heating with zinc dust to 200°, is very evident:—



$$C_6H_4\left\langle\begin{matrix}CO.Cl\\CO.Cl\end{matrix}\right. + C_6H_6 = C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle C_6H_4 + 2HCl;$$

as well as its production from ortho-benzoyl benzoic acid when the latter is heated with phosphoric anhydride (*Berichte*, 7, 578):—



$$C_6H_4\left\langle\begin{matrix}CO.C_6H_5\\CO.OH\end{matrix}\right. = C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle C_6H_4 + H_2O;$$

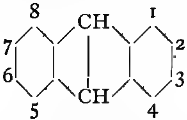
and by the distillation of calcium phthalate. In this manner the homologous alkyl anthraquinones are obtained from the homologous *o*-benzoyl benzoic acids.

o-Benzoyl benzoic acid is directly converted into anthracene upon heating it with zinc dust, and *o*-toluyl benzoic acid (p. 864) yields β-methyl anthracene (*Berichte*, 19, Ref. 686).

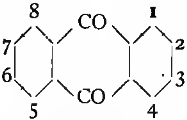
Again, when *o*-tolyl-phenyl ketone,  $C_6H_4\left\langle\begin{matrix}CO.C_6H_5\\CH_3\end{matrix}\right.$ (p. 862), is heated with lead oxide, anthraquinone is produced. If zinc dust be employed anthracene results. In the same manner anthracene is formed from orthotolyl-phenyl methane, $C_6H_4(CH_3).CH_2.C_6H_6$, and methyl anthracene, etc., from *o*-ditolyl-methane, $C_6H_4(CH_3).CH_2.C_6H_4.CH_3$, etc. (*Berichte*, 23, Ref. 198).

It follows from all these syntheses (by means of ortho-derivatives of benzene), that in one of the benzene nuclei of anthracene and its derivatives, the two carbon-atoms are inserted in the ortho-position; that this is true, too, of the second nucleus is inferred from the production of anthracene and its hydride from *o*-brom-benzyl bromide (p. 893); also from the behavior of oxanthraquinone, $C_6H_4.(CO)_2C_6H_3.OH$, which is synthesized from brom-ortho-benzoyl benzoic acid, $C_6H_5.CO.C_6H_3Br.CO_2H$ (from brom-phthalic acid), and when oxidized (the second benzene nucleus being destroyed) yields phthalic acid, $C_6H_4(CO_2H)_2$ (*Berichte*, 12, 2124).

Therefore, anthracene and its derivatives possess a symmetrical constitution, corresponding to the symbols:—



Anthracene.



Anthraquinone.

in which the numbers designate the eight affinities of the two benzene nuclei. The positions 1, 4, 5, 8 are alike, also 2, 3, 6, 7; the former (as with naphthalene, see this) are called the α-, the latter the β-positions. We conclude, then, that if one hydrogen atom of the benzene ring be replaced two isomeric mono-derivatives (α and β) of anthracene and anthraquinone can be formed; whereas by the entrance of two similar substituting groups ten isomeric di-derivatives result (p. 898). By the replacement of the middle hydrogen atoms of anthracene other isomerides are obtained, which have been termed γ-derivatives or *meso*-derivatives (*Berichte*, 18, 690).

The two intermediate carbon atoms of anthracene form, with two carbon atoms from each of the two benzene nuclei, a closed chain consisting of six carbon atoms. It resembles the ring of benzene. Hence anthracene is included among the condensed benzenes (see naphthalene). In most of the transformations of anthracene the intermediate carbon atoms are first attacked.

Anthracene, $C_{14}H_{10}$, is formed, in addition to the syntheses given, from many carbon compounds when they are exposed to a high heat, and for that reason it is produced in larger quantities in coal-tar.

Pure anthracene is obtained from the commercial product (boiling at 340–360°) by crystallization from hot xylene and alcohol, or by extraction with acetic ester or carbon disulphide (*Annalen*, 191, 288); but better by crystallization from pyridine (*Berichte*, 21, Ref. 75). Or, hydranthranol is first obtained from anthraquinone (p. 896) and then boiled with water (*Journ. prac. Chemie*, 23, 146; *Berichte*, 18, 3034).

Anthracene crystallizes in colorless monoclinic tables, showing a beautiful blue fluorescence. It dissolves with difficulty in alcohol and ether, but easily in hot benzene. It melts at 213°, and distils above 360°. Picric acid in benzene solution unites with it, yielding $C_{14}H_{10}.2C_6H_3(NO_2)_3O$, crystallizing in red needles, and melting at 170°.

When the cold saturated solution of anthracene in benzene is exposed to sunlight, a modification of anthracene, *Para-anthracene*, $C_{14}H_{10}$, separates out in plates. It dissolves with difficulty in benzene, is not attacked by nitric acid or bromine, melts at 244°, and in so doing reverts to common anthracene.

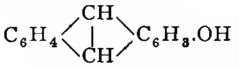
Anthracene Dihydride, $C_{14}H_{12}$, results from the action of sodium amalgam upon the alcoholic solution of anthracene. It melts at 107°, and boils at 305°. When heated with hydriodic acid and amorphous phosphorus to 220° **Anthracene hexahydride**, $C_{14}H_{16}$, results. It melts at 63°, and boils at 290°. **Anthracene perhydride**, $C_{14}H_{24}$, is another product. It melts at 88°, and boils at 270° (*Berichte*, 21, 2510).

Mono- and di-halogen anthracenes are obtained when chlorine and bromine act upon anthracene (in CS_2 solution). The two middle carbon atoms are substituted. **Nitroanthracene** could not be obtained. Nitric acid (concentrated and diluted, and also in alcoholic solution) oxidizes it to anthraquinone and dinitroanthraquinone.

β-**Amido-anthracene**, $C_{14}H_9.NH_2$, called anthramine, is formed on heating β-anthrol (see below) with alcoholic ammonia to 170°. It forms yellow leaflets, melting at 237°. **Meso-amido-anthracene**, $C_6H_4(C_2H.NH_2)C_6H_4$, is prepared by heating anthranol with ammonia. Golden yellow leaflets, decomposing at 115° (*Berichte*, 23, 2523).

When anthracene is dissolved in sulphuric acid two **Disulphonic Acids**, $C_{14}H_8(SO_3H)_2$ (α and β), are produced. These, fused with caustic potash, yield two dioxy-anthracenes and also the corresponding dioxyanthraquinones.

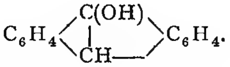
Oxy-anthracenes, $C_{14}H_9.OH$:—



$C_6H_4\left\langle\begin{matrix}CH\\ |\\ CH\end{matrix}\right\rangle C_6H_3.OH$

Anthrol.

and



$C_6H_4\left\langle\begin{matrix}C(OH)\\ |\\ CH\end{matrix}\right\rangle C_6H_4.$

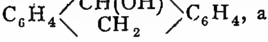
Anthranol.

Two isomeric compounds (α and β) correspond to the first formula; they are phenols and are called *anthrols*. β-**Anthrol** has been obtained from anthracenesulphonic acid (from β-anthraquinone sulphonic acid) and by the reduction of oxyanthraquinone. It crystallizes in leaflets, dissolving with a yellow color in the alkalies, and in sulphuric acid with a blue color when heated. After the introduction of the acetyl group in OH (compare oxidation of phenols, p. 686) chromic acid and acetic acid oxidize it to oxyanthraquinone.

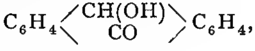
Anthranol has the second formula; it is produced by the careful reduction of anthraquinone with tin and acetic acid (*Berichte*, 20, 1854). It crystallizes from alcohol in shining needles, melting with decomposition at 165°. Chromic acid oxidizes it to anthraquinone. Hydroxylamine converts it into anthraquinone oxime (*Berichte*, 20, 613). For additional derivatives see *Berichte*, 21, 1176.

The reduction of anthraquinone with zinc dust yields

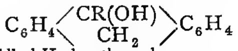
Hydranthranol,



$C_6H_4\left\langle\begin{matrix}CH(OH)\\ CH_2\end{matrix}\right\rangle C_6H_4$, and



$C_6H_4\left\langle\begin{matrix}CH(OH)\\ CO\end{matrix}\right\rangle C_6H_4$, Oxanthranol. These form *alkyl compounds* with caustic potash and the alkylogens (*Berichte*, 18, 2150):—



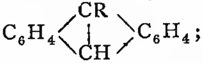
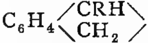
$$C_6H_4\left\langle\begin{matrix}CR(OH)\\CH_2\end{matrix}\right\rangle C_6H_4$$

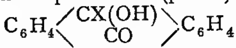
Alkyl Hydranthranols.

and

$$C_6H_4\left\langle\begin{matrix}CR(OH)\\CO\end{matrix}\right\rangle C_6H_4.$$

Alkyl-oxanthranols.

The former, when boiled with hydrochloric acid, part with water and yield *alkyl anthracenes*,  $C_6H_4\left\langle\begin{matrix}CR\\|\\CH\end{matrix}\right\rangle C_6H_4$; the latter are also reduced to alkyl anthracenes by zinc dust, but with hydriodic acid to alkyl anthra-hydrides,  $C_6H_4\left\langle\begin{matrix}CRH\\CH_2\end{matrix}\right\rangle C_6H_4$, etc. (*Annalen*, 212, 67).

Derivatives of anthranol, in which the hydrogen of the CH-group is replaced by *phenyls*, are the so-called *phthalidins* and appear on mixing the triphenyl-carboxylic acids with sulphuric acid (p. 880). When oxidized they pass into phenyl-oxanthranols,  $C_6H_4\left\langle\begin{matrix}CX(OH)\\CO\end{matrix}\right\rangle C_6H_4$ (the phthalideïns) and yield phenyl anthracene (p. 901), if ignited with zinc dust. **Phenyl anthranol** resembles anthranol, and melts at 141–144°. **Benzyloxanthranol** is described in *Berichte*, 23, 2527.

Dioxyanthracenes, $C_{10}H_8(OH)_2$. Of the ten possible isomeric diphenols (pp. 894 and 898), two with the formula, $HO.C_6H_3.C_2H_2.C_6H_3.OH$, have been derived from the two anthracene disulphonic acids by fusion with caustic potash. By oxidizing their acetates with chromic acid (see above) and saponifying, they yield the corresponding dioxyanthraquinones; the β-compound (called chrysazol) yields chrysazin, the α-compound (rufol) anthrarufin (p. 900). A third (called *flavol*) is obtained from β-anthraquinone-disulphonic acid.

Anthraquinone, $C_{14}H_8O_2 = C_6H_4.C_2O_2.C_6H_4$, Diphenylene diketone (p. 892), is produced very readily, in addition to the synthetic methods given, by oxidizing anthracene, anthrahydride, dichlor- and dibrom-anthracene with nitric or chromic acid. We can obtain it by adding pulverized potassium bichromate to a hot glacial acetic acid solution of anthracene (*Annalen*, Sup., 7, 285) or with less expense by oxidation with the theoretical amount of a chromic acid mixture.

Anthraquinone sublimes in yellow needles, melting at 277°, and is soluble in hot benzene and nitric acid. It is very stable, and is altered with difficulty by oxidizing agents. Sulphurous acid does not reduce it (unlike the true quinones, v. p. 698).

It reverts to anthracene if heated to 150° with hydriodic acid, or with zinc dust and ammonia. When fused with potassium hydroxide (at 250°), it decomposes into two molecules of benzoic acid; heated with soda-lime it yields benzene and a little diphenyl. By its union with one molecule of hydroxylamine it forms anthraquinone-oxime, $C_{14}H_8O(N.OH)$, subliming at 200°.

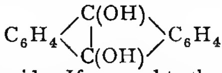
When anthraquinone is digested with bromine at 100° it becomes **Dibrom-anthraquinone**, $C_{14}H_6Br_2O_2$, subliming in yellow needles. It is more easily obtained by oxidizing with nitric acid; dichloranthraquinone is similarly formed.

It yields alizarin if heated to 160° with caustic potash. A **monobrom-anthraquinone** (β) has been obtained from tribrom-anthracene by oxidation, and melts at 187°.

Dinitroanthraquinone, $C_{14}H_6(NO_2)_2O_2$, is formed (with anthraquinone) on digesting anthracene with dilute nitric acid (1 part with 3 parts water). It consists of yellow needles or leaflets, melting at 280°, and like picric acid manifests the property of forming crystalline combinations (Fritsche's Reagent) with many hydrocarbons. The **mononitroquinone** is obtained when anthraquinone is boiled with concentrated nitric acid. It is a light yellow powder, melting at 230° (*Berichte*, 16, 363). Various dyes are obtained from it through the action of sulphuric acid (*Berichte*, 17, 891).

Heated to 250–260° with concentrated sulphuric acid anthraquinone yields β-**Anthraquinone-mono-sulphonic acid,** $C_{14}H_7O_2.SO_3H$, which crystallizes from water in yellow leaflets; fused with potassium hydroxide it forms oxanthraquinone. Protracted heating with 4–5 parts sulphuric acid yields two **disulphonic acids,** $C_{14}H_6O_2(SO_3H)_2$ (α and β). The first may be synthesized by heating *o*-benzoyl benzoic acid (p. 863) with fuming sulphuric acid. Fused with potassium hydroxide it yields anthraflavic acid (2OH) and flavopurpurin (3OH), while the second furnishes isoanthraflavic acid (2OH) and anthrapurpurin (3OH). Two isomeric **Anthraquinone-disulphonic Acids** (γ and δ) are obtained from the two anthracene-disulphonic acids by oxidation with nitric acid, and if fused with caustic potash yield chrysazin and anthrarufin; trioxyquinone is produced simultaneously, together with oxychrysazin and oxyanthrarufin (p. 898).

Anthraquinone is reduced, when digested with zinc dust and an alkaline hydroxide, to

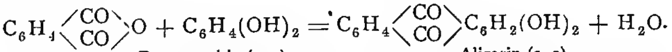


Anthrahydroquinone, $C_6H_4\left\langle\begin{matrix}C(OH)\\ | \\ C(OH)\end{matrix}\right\rangle C_6H_4$, which is precipitated in yellow flakes by hydrochloric acid. If exposed to the air it again oxidizes to anthraquinone.

The **Oxyanthraquinones,** corresponding to the phenols, are derived by introducing hydroxyl into anthraquinone. There are two mono-oxy-anthraquinones, $C_6H_4.C_2O_2.C_6H_3.OH$ (α and β) and ten dioxy-anthraquinones (p. 894); the latter are important as dyes. They originate from the brom (chlor) anthraquinones and the sulphonic acids on fusion with alkalies, when the substituting groups are replaced by hydroxyls.

By stronger fusion there generally ensues an additional entrance of hydroxyl (oxy- and dioxyanthraquinones result from the mono-sulphonic acid); the same is true in the fusion of the oxy-quinones—but, as it appears, this is only true for those derivatives which contain but one hydroxyl in each benzene nucleus (*Berichte*, 11, 1613).

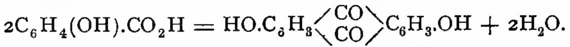
The oxyanthraquinones (like anthraquinone) may be synthetically prepared on heating phthalic anhydride with phenols (mono- and poly-valent) and sulphuric acid to 150° (p. 881):—



$$C_6H_4\left\langle\begin{matrix}CO\\ CO\end{matrix}\right\rangle O + C_6H_4(OH)_2 = C_6H_4\left\langle\begin{matrix}CO\\ CO\end{matrix}\right\rangle C_6H_2(OH)_2 + H_2O.$$

Pyrocatechin (1, 2). Alizarin (1, 2).

The di- and tetra-oxyquinones are also produced from the oxy- and dioxybenzoic acids, when heated with sulphuric acid, but it seems only the meta derivatives are reactive (*Berichte*, 18, 2142). Metaoxybenzoic acid yields three dioxyanthraquinones :—



$$2C_6H_4(OH).CO_2H = HO.C_6H_3\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle C_6H_3.OH + 2H_2O.$$

Metaoxybenzoic Acid. Dioxyanthraquinone.

Continued fusion with alkalies causes the oxyanthraquinones to separate into their component oxybenzoic acids (same as anthraquinone decomposes into benzoic acid) and this reaction aids in the determination of the position of the isomerides (*Berichte*, 12, 1293).

Individual hydroxyls in the oxyanthraquinones are reduced by heating the latter with stannous chloride and sodium hydroxide (*Annalen*, 183, 216). Heated to 150–200° with ammonia water single OH-groups are replaced by amide groups; these are further eliminated by diazotizing (*Annalen*, 183, 202). All anthraquinones are reduced to anthracene when heated with zinc dust.

Oxyanthraquinones, $C_{14}H_8O_3 = C_{14}H_7(O_2).OH$.

Ordinary **Oxyanthraquinone** (β) is obtained from brom-anthraquinone and anthraquinone-sulphonic acid, and also from phthalic anhydride with phenol (together with erythro-oxyanthraquinone). It crystallizes in sulphur-yellow needles, melting at 302°, and sublimes in leaflets. Isomeric **erythro-oxyanthraquinone** (a) forms yellow needles, melting at 173–180°, and sublimes at 150°. Both oxyanthraquinones yield dioxyanthraquinone (alizarin), when fused with caustic potash.

Dioxyanthraquinones, $C_{14}H_8O_4 = C_{14}H_6(O_2)(OH)_2$.

The ten possible isomerides (p. 894) are known. Four of them contain the 2OH-groups in one and the same benzene nucleus: alizarin (from pyrocatechin) has the structure (2, 2), purpur-oxyanthin is (1, 3), quinizarin (from hydroquinone) is (1, 4); and hystazarin is (2, 3).

Only those dioxy- and polyoxyanthraquinones possess distinct coloring-power, in which the two *free* hydroxyls occupy the position (1, 2) (*Berichte*, 21, 435, 1164). Consult *Berichte*, 19, 2327 for the spectra of the dioxyanthraquinones.

1. **Alizarin**, dioxyanthraquinone (1, 2), is the coloring ingredient of the root of the madder (*Rubia tinctorium*), in which it is contained as *ruberythric acid* (identical with morindin from *Morinda citrifolia*). Through the action of a ferment in the madder root, ruberythric acid decomposes when boiled with dilute acids or alkalies, or by standing with water, into glucose and alizarin :—

$$C_{26}H_{28}O_{14} + 2H_2O = C_{14}H_8O_4 + 2C_6H_{12}O_6.$$

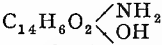
This decomposition into alizarin and glucose takes place in the madder root even when it is allowed to lie exposed to the air for some time. This was the basis for obtaining alizarin formerly, and of the application of madder root in dyeing. Later, different madder preparations were employed, in which the conversion into alizarin was more complete. Thus *garancin* was obtained by treating madder root with sulphuric acid, which decomposes the ruberythic acid, but does not alter the alizarin produced. At present artificial alizarin is employed almost exclusively.

Artificial alizarin was first obtained by Graebe and Liebermann, in 1868, when they heated dibrom-anthraquinone with potassium hydroxide. It is also produced from dichlor- and monobrom-anthraquinone, from the two oxy-anthraquinones and anthraquinone sulphonic acid, by fusion with caustic-potash at 250–270°. At present it is manufactured on a large scale by these methods. The fusion is dissolved in water, the alizarin precipitated by hydrochloric acid and purified by recrystallization or sublimation. Alizarin also results on heating phthalic anhydride with pyrocatechin and sulphuric acid (p. 897).

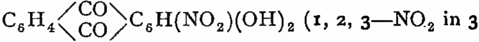
Alizarin crystallizes from alcohol in reddish-yellow prisms or needles, containing three molecules of water, which escape at 100°. It melts at 282°, and sublimes in orange-red needles. It dissolves readily in alcohol and ether, and sparingly in hot water. In concentrated sulphuric acid it dissolves with a dark-red color and is precipitated by water unchanged. Its *diacetate* melts at 160°.

Alizarin is a diphenol, and like the substituted phenols behaves as an acid. It dissolves with a purple-red color in the alkalies; lime and barium salts throw out the corresponding salts as blue precipitates. Alums and tin salts produce red-colored precipitates (madder lakes); while ferric salts form blackish-violet precipitates.

This property of alizarin yielding colored compounds with metallic oxides is the basis of its application in dyeing and cotton printing. The goods are mordanted with alumina (by immersing them in aluminium-acetate, then heating, whereby aluminium hydroxide is deposited on the fibres) and then dipped into the solution of alizarin; the resulting alizarin-aluminate is fixed by the fibres. In dyeing with turkey-red it is customary to mordant the cloth with oil and alum.



Alizarin-amide, $C_{14}H_6O_2\langle{}^{NH_2}_{OH}$, obtained by heating alizarin with water to 200°, crystallizes in needles, having metallic lustre, melts at 225° and sublimes. Heated with hydrochloric acid to 250°, or by fusion with potassium hydroxide, it yields alizarin; when diazotized it changes to oxyanthraquinone (p. 897).



β-**Nitro-alizarin,** $C_6H_4\langle{}^{CO}_{CO}\rangle C_6H(NO_2)(OH)_2$ (1, 2, 3—NO_2 in 3), *Alizarin-orange*, is produced by the action of vapors of hyponitric acid (NO_2) upon alizarin, or of nitric acid upon the glacial acetic acid solution (*Berichte*, 12, 584). It crystallizes from chloroform in orange-red leaflets with green reflex, and melts at 244°. It dissolves in alkalies with a violet-red color, and forms lakes.

It yields phthalic acid when oxidized with nitric acid. Isomeric *a-nitro-alizarin* (1, 2, 4) is obtained by the nitration of diaceto-alizarin. It melts at 195°, and passes readily into purpurin.

β-**Amido-alizarin** results by the reduction of β-nitroalizarin. Acetic anhydride converts it into an ethenyl compound, which proves that the amido-group occupies an ortho position relatively to a hydroxyl group (*Berichte*, 18, 1666).

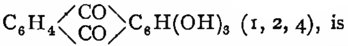
When β-nitro-alizarin is heated with glycerol and sulphuric acid to 100° we obtain *alizarin-blue*, $C_{17}H_9NO_4$, a derivative of anthraquinoline (see this) (*Berichte*, 18, 447).

Of the alizarin isomerides (p. 897) **quinizarin** (1, 4), **purpuroxanthin** (1, 3), and **hystazarin** (2, 3) (*Berichte*, 21, 2501) contain both hydroxyls in one benzene nucleus—whereas **anthraflavic acid, iso-anthraflavic acid, metabenzdioxyanthraquinone** (from *m*-oxybenzoic acid, p. 897), **anthrarufin** and **chrysazin** have the two hydroxyls in the two benzene nuclei.

Chrysazin is obtained from its tetranitro-compound, $C_{14}H_2(NO_2)_4(O_2)(OH)_2$, the so-called **chrysammic acid**, by reduction and the replacement of the amid-groups. This latter acid is obtained when aloës are digested with concentrated nitric acid.

Trioxyanthraquinones, $C_{14}H_5O_2(OH)_3$.

These are produced on oxidizing dioxyanthraquinones or upon fusing them with alkalies (p. 897).

1. **Purpurin**,  $C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle C_6H(OH)_3$ (1, 2, 4), is present with alizarin in the madder root, and is separated from it by a boiling alum solution, which does not dissolve the latter. It is prepared artificially by heating alizarin and quinizarin with manganese dioxide and sulphuric acid to 150°; purpuroxanthin is oxidized to purpurin by simply exposing its alkaline solution to the air. It is also obtained from tribrom-anthraquinone. Purpurin crystallizes with one molecule of water, in reddish-yellow needles or prisms, which, at 100°, lose water and then sublime. It dissolves with a pure red color in hot water, alcohol, ether and the alkalies. Lime and baryta water yield purple-red precipitates. Cloth previously acted on by mordants is dyed the same as by alizarin. It oxidizes to phthalic and oxalic acids when boiled with nitric acid; it yields anthracene upon distillation with zinc dust. Its *triacetate* melts at 190–193°.

Purpurin-amide, $C_{14}H_5O_2(OH)_2NH_2$ (see alizarinamide, p. 899), is obtained on digesting purpurin with aqueous ammonia at 150°; it crystallizes in brownish-green needles, with metallic lustre, and passes into purpuroxanthin by the replacement of the amido-group by hydrogen.

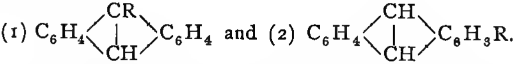
Flavopurpurin, anthrapurpurin and **oxy-chrysazin** are isomerides of purpurin. See *Berichte*, 21, 1164, for their ethers.

Its tetraoxyanthraquinones, $C_6H_2(OH)_2.(C_2O_2)C_6H_2(OH)_2$, are the so-called **anthrachrysone**, obtained by heating symmetrical dioxybenzoic acid with sulphuric acid (p. 898), and **rufiopin**, $C_{14}H_8O_6$, obtained from opianic acid (p. 794) and proto-catechuic acid with sulphuric acid. Both yield anthracene when heated with zinc dust.

A Pentaoxyanthraquinone, $C_{14}H_8O_7 = C_6H_2.(OH)_2(CO)_2C_6H(OH)_3$, is formed (together with anthrachrysone and rufigallic acid) when gallic acid and symmetrical dioxybenzoic acid are heated with sulphuric acid (*Berichte*, 19, 751).

Rufigallic Acid, $C_{14}H_8O_8 + 2H_2O$, is a hexa-oxy-anthraquinone, which is formed when gallic and digallic acids are heated with sulphuric acid. It consists of reddish-brown crystals, losing water at 120°, and subliming in red needles. It dissolves with an indigo-blue color in concentrated potassium hydroxide. Sodium amalgam reduces it to alizarin.

Alkylic Anthracenes:—



$$(1)\ C_6H_4\left\langle\begin{matrix}CR\\|\\CH\end{matrix}\right\rangle C_6H_4 \quad\text{and}\quad (2)\ C_6H_4\left\langle\begin{matrix}CH\\|\\CH\end{matrix}\right\rangle C_6H_3R.$$

γ-Derivatives. α- and β-Derivatives.

The derivatives of the first type, called γ-derivatives, meso-derivatives, are produced from the alkyl hydranthranols (p. 896), on boiling with alcohol and some hydrochloric acid or picric acid. They unite to characteristic compounds with picric acid (*Annalen*, 212, 100).

γ-**Ethyl-anthracene**, $C_{14}H_9(C_2H_5)$, melts at 60°, **isobutyl-anthracene** at 57°, and **amyl-anthracene** at 59°. Chromic acid oxidizes the last to amyl-oxyanthranol. The **phenyl anthracene**, $C_{14}H_9(C_6H_5)$, corresponding to these alkyl derivatives, is obtained from phenyl anthranol (p. 896), on ignition with zinc dust. It melts at 152°.

Compounds of the formula 2 can exist in two isomeric forms (α and β). At present but one methyl anthracene is known.

Methyl-anthracene, $C_{14}H_9.CH_3$, is obtained on conducting the vapors of ditolyl-methane and ditolyl-ethane through a red-hot tube (p. 893); also on heating emodin (see below), and chrysophanic acid with zinc dust, as well as by prolonged boiling of benzoyl xylene, $C_6H_5.CO.C_6H_3(CH_3)_2$. It occurs in crude anthracene, and is obtained from oil of turpentine on exposure to a red heat. It resembles anthracene, crystallizes from alcohol in yellow leaflets, and melts at 190°. It yields a crystalline compound with picric acid, and this consists of dark-red needles. Anthraquinone-carboxylic acid is produced when methyl-anthracene, dissolved in glacial acetic acid, is oxidized by chromic acid. Concentrated nitric acid converts it into **Methyl-anthraquinone**, which is also present in crude anthraquinone, and melts at 177°.

Chrysophanic Acid, $C_{14}H_5(CH_3)(O_2)(OH)_2 = C_{15}H_{10}O_4$, **Rheïnic Acid**, is the dioxyquinone of methyl anthracene. It exists in the lichen *Parmelia parietina*, in the senna leaves (of the Cassia varieties) and in the root of rhubarb (from the *Rheum* variety), from which it may be extracted by means of ether or alkalies. It crystallizes in golden yellow needles or prisms, melting at 162°, and subliming with partial decomposition. It dissolves in alkalies with a purple-red color. Zinc dust reduces it to methyl anthracene.

Chrysarobin, $C_{30}H_{26}O_7$, a reduction product of chrysophanic acid, occurs in in goa- and arroroba-powder. It is a yellow-colored powder. Air oxidizes its alkaline solution to chrysophanic acid. The same occurs in the animal organism (*Berichte*, 21, 447).

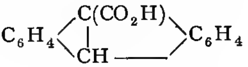
Methyl-alizarin, $C_{15}H_{10}O_4$, is an isomeric dioxymethylanthraquinone. It is obtained by fusing methyl-anthraquinone sulphonic acid with alkalies. It is very similar to alizarin, melting at 250–252°, and readily subliming in red needles. In alkalies it dissolves with a bluish-violet color.

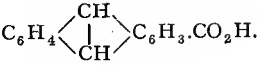
Emodin, $C_{15}H_{10}O_5 = C_{14}H_4(CH_3)O_2(OH)_3$, is a trioxy-quinone of methyl anthracene. It occurs with chrysophanic acid in the bark of wild cherry and in the root of rhubarb. If distilled with zinc dust it yields methyl-anthracene. It consists of orange-red crystals, melting at 245–250°.

Dimethyl-anthracene, $C_{14}H_8(CH_3)_2$, has been obtained from the portions of aniline oil boiling at high temperatures. It consists of shining leaflets, melting at 224–225°. If oxidized it yields a quinone and a mono- and dicarboxylic acid. Isomeric **dimethyl anthracenes** have been obtained from xylyl chloride, $C_6H_4(CH_3).CH_2Cl$, on heating it with water (melting at 200°), from toluene and CH_2Cl_2 with $AlCl_3$ (M. P. 225°) and from ethylidene chloride, $CH_3.CHCl_2$, and benzene with $AlCl_3$. The latter contains the two methyl groups linked to the two intermediate carbon atoms, and melts at 179°.

See *Berichte*, 20, 1364, upon the *dimethyl anthraquinones*, $C_{14}H_6O_2(CH_3)_2$.

Anthracene Carboxylic Acids:—


γ-Acid.


α- and β-Acid.

γ-**Anthracene Carboxylic Acid** (its chloride) is formed when anthracene is heated with phosgene to 200° (*Berichte*, 20, 701). It is sparingly soluble in hot water, readily in alcohol, crystallizes in yellowish needles, and melts at 206°, with decomposition into carbon dioxide and anthracene. Chromic acid in acetic acid solution oxidizes it to anthraquinone.

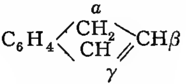
The α- and β-acids are formed from the anthracene-mono-sulphonic acids by means of the cyanides, and from the anthraquinone carboxylic acids by reduction with ammonia and zinc dust; the α-acid melts at 260°, the β-acid at 280°.

The **anthraquinone carboxylic acids**, $C_6H_4(C_2O_2)C_6H_3.CO_2H$, are produced by oxidizing the α- and β-carboxylic acids and methyl-anthraquinone with chromic acid in acetic acid. Both melt at 285°.

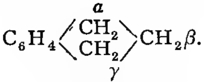
Pseudo-purpurin, $C_{15}H_8O_7 = C_{14}H_4O_2(OH)_3.CO_2H$, purpurin carboxylic acid, occurs in crude purpurin (from madder), and crystallizes from chloroform in red leaflets, melting at 218–220°. Further heating to 180° or boiling with caustic potash decomposes it into carbon dioxide and purpurin.

Indene and Hydrindene Group.

Indene and *Hydrindene* (formerly called indonaphthene and hydrindonaphthene) may be considered the transition members from benzene to naphthalene. They contain besides the benzene ring, a five-membered carbon ring (two C-atoms in common with the benzene nucleus), hence may be compared with indol and hydrindol (p. 827) with which they have many analogies (see Roser, *Annalen*, 247, 129)*:—



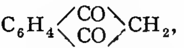
Indene.



Hydrindene.

The following keto-derivatives attach themselves to the preceding:—


Indone.


etc.

αγ-Diketohydrindene.

1. **Indene**, C_9H_8, occurs together with coumarone (p. 825) in that fraction of coal-tar boiling at 176°–182°. After the removal of naphthalene, it can be extracted as a picric acid compound (*Berichte*, 23, 3276). It is a clear oil, boiling at 177–178°; its sp. gr. = 1.040 at 15°. It resembles coumarone; sulphuric acid converts it into a resin. Bromine converts it into a dibromide, $C_9H_8Br_2$, that melts at 44°. Sodium in absolute alcohol reduces it to *hydrindene*, C_9H_{10} (see above), boiling at 176°.

γ-**Methyl Indene**, $C_9H_7(CH_3)$, was first prepared from γ-methyl indene carboxylic acid (see below). It is a liquid with an odor resembling that of naph-

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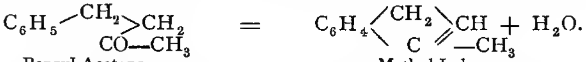
* C. Koenig, Theorie und Geschichte der 5-gliedrigen Kohlenstoffringe.

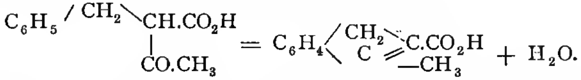
thalene. It boils at 205° (*Annalen*, **247**, 159). It can be directly synthesized (in slight amount) by condensing benzylacetone with sulphuric acid (*Berichte*, **23**, 1882):—



Benzyl Acetone. γ-Methyl Indene.

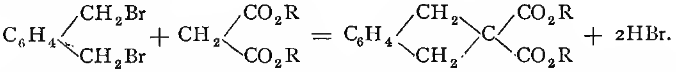
Some derivatives of cinnamic aldehyde deport themselves similarly. Nitro-α-methyl cinnamic aldehyde, $C_6H_4(NO_2).CH:C(CH_3).CHO$, may be reduced to amido-β-methyl indene (*Berichte*, **22**, 1830), and nitro-α ethyl cinnamic aldehyde to amido-β-ethyl indene. The reaction is analogous to the formation of the coumarone and indol derivatives.

2. The formation of the carboxyl derivatives of indene (compare the formation of coumarilic acid by the method of Hantzsch, p. 825), proceeds in a manner analogous to the formation of alkyl indenes. Thus, benzylacetoacetic ester readily changes, when digested with sulphuric acid, to *γ-methyl indene-β-carboxylic acid* (*Berichte*, **20**, 1574; *Annalen*, **247**, 157):—

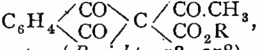


It melts at 200°, and decomposes further into carbon dioxide and γ methyl indene (see above).

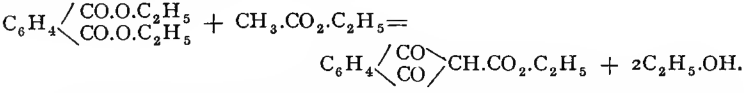
3. The *hydrindene* derivatives have been obtained in the same manner as the tetra- and pentamethylene derivatives (p. 578): by the action of *o*-xylylene bromide (p. 573) upon malonic ester and sodium alcoholate (Baeyer and Perkin, *Berichte*, **17**, 125):—

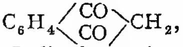


The resulting ether is saponified, and we then obtain **Hydrindo-naphthene Dicarboxylic Acid**, $C_9H_8(CO_2H)_2$, melting at 199°, and decomposing into carbon dioxide and **hydrindene carboxylic acid**, $C_9H_9.CO_2H$, which melts at 130°, and distils without decomposition.

The latter is also produced by the saponification of *acetyl hydrindene-carboxylic ester*, , obtained from *o*-xylylene bromide and aceto-acetic ester (*Berichte*, **18**, 378). Potassium permanganate oxidizes hydrindene carboxylic acid to carbophenyl glyoxylic acid (p. 765).

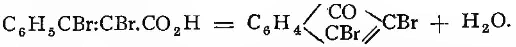
4. *Keto-derivatives* of indene and hydrindene result (1) by condensing phthalic esters and fatty acid esters with sodium (W. Wislicenus, *Berichte*, **21**, Ref. 642; *Annalen*, **246**, 347):—



The *diketohydrindene-carboxylic ester* thus formed melts at 75–78°, and readily decomposes into *αγ-diketohydrindene*, , colorless needles, melting at 129–131° with decomposition. It dissolves quite easily in dilute alkalies with an intense yellow color (*Berichte*, **22**, Ref. 581; *Annalen*, **252**, 72).

Phthalic acid ester and propionic ester yield *β-Methyl-diketohydrindene*, $C_6H_4(CO)_2CH.CH_3$, melting at 85° (*Berichte*, 22, 581).

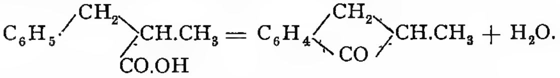
(2) By the inner condensation of cinnamic acid derivatives, aided by sulphuric acid. Thus, dibromindone is derived from β-dibromcinnamic acid (p. 810) (Roser, *Annalen*, 247, 140):—



$$C_6H_5CBr{:}CBr.CO_2H = C_6H_4\left\langle\begin{array}{c}CO\\CBr\end{array}\right\rangle CBr + H_2O.$$

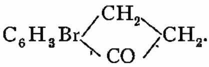
Dibromindone, $C_9H_4Br_2O$, consists of orange-yellow colored needles, with an odor resembling that of quinone. It volatilizes quite readily with steam, and melts at 123°.

Hydrindone could not be obtained from hydrocinnamic acid in this way; α-methyl hydrocinnamic acid (p. 814), on the contrary, passes very readily into *β-methyl hydrindone* (v. Miller, *Berichte*, 23, 1888):—

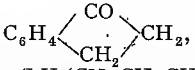


$$C_6H_5.CH_2.\underset{\displaystyle CO.OH}{CH}.CH_3 = C_6H_4\left\langle\begin{array}{c}CH_2\\CO\end{array}\right\rangle CH.CH_3 + H_2O.$$

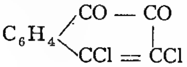
m- and *p-*Bromhydrocinnamic acids yield in this way *m-* and *p-bromhydrindone*,



$$C_6H_3Br\left\langle\begin{array}{c}CH_2\\CO\end{array}\right\rangle CH_2.$$

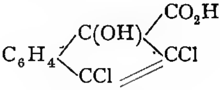
Hydrindone,  $C_6H_4\left\langle\begin{array}{c}CO\\CH_2\end{array}\right\rangle CH_2$, has been prepared by saponifying *o*-cyanbenzyl-acetic ester, $C_6H_4(CN).CH_2.CH_2.CO_2R$, with hydrochloric acid (*Berichte*, 22, 2019); also by distilling calcium *o*-hydrocinnamic carboxylate. Hydrindone forms colorless crystals, with an odor like that of phthalide. It melts at 40° and boils about 244°. Its *oxime* melts at 146°; the *hydrazone* at 120°.

(3) The formation of ketoindene derivatives from naphthalene derivatives is rather remarkable; a six-membered benzene-ring is rearranged to a ring of five members—similar to the production of pentamethylene derivatives from the benzenes, or diphenylene glycollic acid from phenanthraquinone. This change occurs by the action of chlorine or hypochlorous acid upon the naphthols, and naphthoquinones, amidonaphthols, etc. The first product consists of naphthalene keto-derivatives with the groups —CO.CO— or CO.CCl_2—; these sustain the decomposition (Zincke, *Berichte*, 20, 1265, 2890; 21, 2379, 2719). Thus dichlor-β-naphthoquinone and water yield first dichlorindene oxycarboxylic acid, which by oxidation (with elimination of carbon dioxide and two hydrogen atoms) forms dichlorindone:—



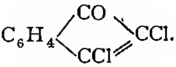
$$C_6H_4\left\langle\begin{array}{l}CO - CO\\ \qquad\quad\;\; |\\ CCl = CCl\end{array}\right.$$

Dichlor-β-naphthoquinone.



$$C_6H_4\left\langle\begin{array}{c}C(OH)\\CCl\end{array}\right\rangle C\begin{array}{l}CO_2H\\Cl\end{array}$$

Dichlorindene-oxycarboxylic Acid.



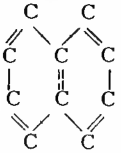
$$C_6H_4\left\langle\begin{array}{c}CO\\CCl\end{array}\right\rangle CCl.$$

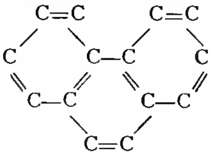
Dichlorindone.

Dichlorindone, $C_9H_4Cl_2O$, resembles dibromindone perfectly, and like the latter is produced by the inner condensation of dichlorcinnamic acid, $C_6H_5.CCl{:}CCl.CO_2H$ (from phenyl propiolic acid). It consists of golden yellow needles, with an odor like that of quinone. It melts at 90° (*Berichte*, 20, 1265).

4. DERIVATIVES WITH CONDENSED BENZENE NUCLEI.

The hydrocarbons belonging here contain two or more benzene nuclei so combined that every two nuclei have two adjoining carbon atoms in common, as seen in the following structural formulas of the nuclei of naphthalene, $C_{10}H_8$, and phenanthrene, $C_{14}H_{10}$:—


Naphthalene Nucleus.


Phenanthrene Nucleus.

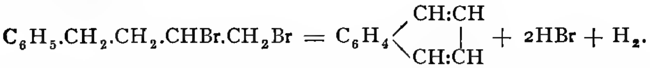
Phenanthrene, with three benzene rings, can also be considered as a diphenyl, $C_6H_5—C_6H_5$, in which two carbon atoms, C=C, in union with each other are inserted in the two ortho-positions of the two benzene nuclei, in such a manner that a third benzene ring is the result.

Pyrene, $C_{16}H_{10}$, *Chrysene*, $C_{18}H_{12}$, *Picene*, $C_{22}H_{14}$, also *acenaphthene*, $C_{14}H_{10}$, *fluoranthene*, $C_{15}H_{10}$, and other hydrocarbons have a similar structure; they are all found in those portions of coal-tar which boil at high temperatures.

1. NAPHTHALENE GROUP.

Naphthalene, $C_{10}H_8$, the parent substance of this group shows the greatest similarity to benzene in its entire deportment. Like benzene it is produced by the action of intense heat upon many carbon compounds, especially if they be conducted, in form of vapor, through tubes raised to a red heat. It is, therefore, present in coal-tar. Numerous derivatives are obtained from it by the replacement of its hydrogen atoms. Only the most important of these will be mentioned.* But few direct synthetic methods are known at present for naphthalene or its derivatives:—

(1) It is derived from phenylene butylene, $C_8H_5.CH_2.CH_2.CH{:}CH_2$, and its dibromide, on leading their vapors over heated lime. The side-chain of four carbon atoms closes, forming a benzene ring:—

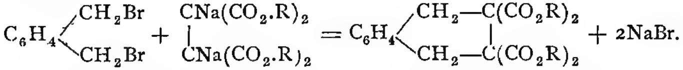


$$C_6H_5.CH_2.CH_2.CHBr.CH_2Br = C_6H_4\left\langle\begin{matrix}CH{:}CH\\ |\\ CH{:}CH\end{matrix}\right. + 2HBr + H_2.$$

---

* See, further, Reverdin and Nölting, Ueber die Constitution des Naphtalins, 2 Aufl., 1887.

(2) A direct synthesis of the second benzene ring also ensues in a manner analogous to the formation of the trimethylene and tetramethylene ring (p. 519), and of the hydrindene ring (p. 902) when *o*-xylylene bromide acts upon disodium-acetylene-tetracarboxylic ester (p. 481) (Baeyer and Perkin, *Berichte*, 17, 448):—

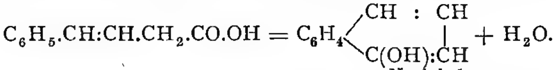


$$C_6H_4\begin{cases}CH_2Br\\CH_2Br\end{cases} + \begin{matrix}CNa(CO_2.R)_2\\|\\CNa(CO_2.R)_2\end{matrix} = C_6H_4\begin{cases}CH_2—C(CO_2R)_2\\ \qquad\quad |\\CH_2—C(CO_2R)_2\end{cases} + 2NaBr.$$

First, we get the ester of tetrahydro-naphthalene-tetracarboxylic acid, and this by saponification yields tetrahydro-naphthalene dicarboxylic acid. Naphthalene results from the distillation of its silver salt. Corresponding experiments with *m*- and *p*-xylylene bromide did not yield ring-shaped chains (*Berichte*, 21, 36; 23, 109).

It is doubtful, according to recent investigations, whether naphthalene derivatives are really produced upon heating benzyl aceto-acetic ester with sulphuric acid (*Berichte*, 20, 1575; 16, 516).

(3) What is further noteworthy is the formation of α-naphthol from phenyl-isocrotonic acid (p. 813), by its elimination of water when boiled (Fittig, *Berichte*, 16, 43):—



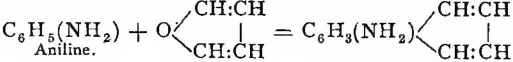
$$C_6H_5.CH:CH.CH_2.CO.OH = C_6H_4\begin{cases}CH\ :\ CH\\ \qquad\quad |\\C(OH):CH\end{cases} + H_2O.$$

α-Naphthol.

Phenylisocrotonic acid is readily obtained from phenyl paraconic acid (p. 793), and the corresponding chlornaphthols are then similarly derived from the chlorphenyl-paraconic acids (*Berichte*, 21, Ref. 733; 21, 3444). α- and β-Methyl paraconic acids yield methyl-α-naphthols (*Berichte*, 23, 96).

Acetyl-α-naphthol is prepared in an analogous manner from β-benzal-lævulinic acid (p. 817).

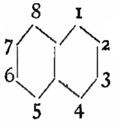
(4) An interesting formation of α-naphthylamine is the condensation of aniline with furfurane upon heating aniline with pyromucic acid and zinc chloride (*Berichte*, 20, Ref. 221):—



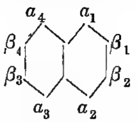
$$\underset{\text{Aniline.}}{C_6H_5(NH_2)} + \underset{\text{Furfurane.}}{O\begin{cases}CH:CH\\ \qquad |\\CH:CH\end{cases}} = \underset{\alpha\text{-Naphthylamine.}}{C_6H_3(NH_2)\begin{cases}CH:CH\\ \qquad |\\CH:CH\end{cases}}$$

Aniline. Furfurane. α-Naphthylamine.

Constitution.—Naphthalene consists of two symmetrically condensed benzene nuclei (p. 905) (Erlenmeyer and Graebe, 1866) and its structure may be expressed by the symbols—

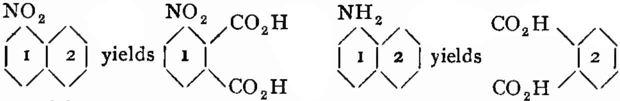


or



in which the numbers indicate the eight affinities of the two benzene nuclei. According to this representation the positions 1, 4, 5 and 8 are of equal value, while the same may be said of 2, 3, 6 and 7 (same as in anthracene and anthraquinone, p. 894); the former are termed the α-positions, the latter the β. It follows, that by the replacement of hydrogen in naphthalene two series of isomeric mono-derivatives, $C_{10}H_7X$ (α and β) can be derived, and with the di-derivatives, $C_{10}H_6X_2$, there are altogether ten isomerides possible.

These inferences relative to the number of isomerides and the accepted structure of the naphthalene nucleus are fully demonstrated by numerous reactions. The presence of a benzene ring in naphthalene follows from its syntheses and from its oxidation to phthalic acid, $C_6H_4(CO_2H)_2$, in which the 2 carbon-atoms of the carboxyl groups occupy the ortho-position. That there is a second benzene ring is shown by the fact that in the destruction of the first ring (by oxidations) phthalic acid or its derivatives are formed. Thus, by destroying the one ring we obtain nitro-phthalic acid, $C_6H_3(NO_2)(CO_2H)_2$, from nitro-naphthalene, $C_{10}H_7(NO_2)$; if, however, we reduce nitronaphthalene to its amide and oxidize the latter, the benzene ring containing the amido group will be obliterated and a benzene derivative—phthalic acid, $C_6H_4(CO_2H)_2$—is again produced:—



Nitronaphthalene. Nitrophthalic Acid. Amido-naphthalene. Phthalic Acid.

The oxidation of the chlorinated naphthalenes led to perfectly analogous results (Graebe, *Annalen*, 149, 20).

The existence of two isomeric series of naphthalene mono-derivatives, $C_{10}H_7X$, indicates the presence of the two different positions (α and β). Atterberg produced (*Berichte*, 9, 1736 and 10, 547) a direct proof that there are four α-positions in naphthalene (two in each benzene nucleus).

That the α-positions correspond to 1 (=4, 5, 8) follows from the fact that the α-derivatives alone are capable of yielding a true quinone (α-naphthaquinone) (Liebermann, *Annalen*, 163, 225). Nölting and Reverdin succeeded in showing that the α-positions were contiguous to the two carbon atoms held in common by both benzene nuclei (*Berichte*, 13, 36). An evidence of this is the formation of α-naphthol from phenyl isocrotonic acid (p. 906). For additional determinations of constitution, consult Erdmann, *Annalen*, 227, 306.

Two adjacent positions (α and β, or 1, 2) in naphthalene have the character of the benzene ortho-position; their derivatives are adapted for the various anhydride formations and ortho-condensations.

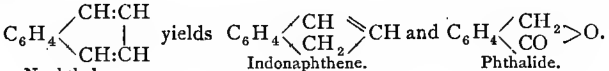
The positions (1, 8) or (4, 5), called the *peri* positions, manifest a similar deportment. They are especially suitable for the production of anhydrides. They differ from the benzene ortho-position in that they incline to the formation of lactones and sulphones (*Berichte*, 22, 3333), and are incapable of yielding a phenazine with phenanthraquinone (see perinaphthylene diamine, p. 913).

Notwithstanding that naphthalene derivatives possess, in a general way, the character of benzene, they yet exhibit many differences. To express this in the formula showing their constitution, E. Bamberger assumes that the two benzene rings in naphthalene are differently constructed from the usual benzene ring, and proposes a formula similar to Baeyer's central benzene formula, with "peculiar potential or central linkages" of the fourth C-valences (*Berichte*, 23, 1124; Ref. 337 and

692; compare Claus, *Jour. prk. Chemie*, 42, 24, 458). According to this idea, the two middle C-atoms of naphthalene are not directly combined, but show two potential or central valences.

Naphthalene, $C_{10}H_8$, occurs in coal-tar, and is obtained by crystallization from that portion boiling from 180–200°. It is purified by distillation with steam and sublimation. It dissolves with difficulty in cold alcohol, readily in hot alcohol and in ether. It crystallizes and sublimes in shining leaves, melting at 79°, and boiling at 218°. It is very easily volatilized, distils with aqueous vapor and possesses a peculiar odor. It forms a crystalline compound, $C_{10}H_8.C_6H_2(NO_2)_3.OH$, with picric acid, which crystallizes from alcohol in needles, melting at 149°. When boiled with dilute nitric acid it is oxidized to phthalic acid. Chromic acid slowly destroys it (p. 783). Nearly all the naphthalene derivatives behave similarly.

Derivatives of indonaphthene (p. 903) and of phthalide are among the intermediate oxidation products of the various naphthalene compounds (*Berichte*, 19, 1156):—



$$C_6H_4\left\langle\begin{matrix}CH{:}CH\\ |\\ CH{:}CH\end{matrix}\right. \text{ yields } C_6H_4\left\langle\begin{matrix}CH\\ CH_2\end{matrix}\right\rangle CH \text{ and } C_6H_4\left\langle\begin{matrix}CH_2\\ CO\end{matrix}\right\rangle O.$$

Naphthalene. Indonaphthene. Phthalide.

Naphthalene Hydrides. Like benzene, naphthalene forms additive products with hydrogen. The di- and tetra-hydrides result from the action of metallic sodium upon its amyl-alcohol solution. Higher derivatives are produced if naphthalene be heated with hydriodic acid or PH_4I and phosphorus.

Naphthalene Dihydride, $C_{10}H_{10}$, is an oil, boiling at 211°. It becomes a solid on cooling, and then melts at +15°

Naphthalene Tetrahydride, $C_{10}H_{12}$, is derived from *ar*-tetrahydro-*a*-naphthylamine by the substitution of its amido-group; its four H-atoms are, therefore, combined in one benzene ring (*Berichte*, 22, 631). It is an oil with an odor resembling that of naphthalene. It boils at 206°.

When naphthalene has had four hydrogen atoms added to one benzene ring, its character is similar to that of the fatty compounds, whereas the non-hydrogenized benzene ring manifests the character of benzene, and the abnormalities which otherwise distinguish the naphthalene nucleus, disappear (p. 907). Tetrahydronaphthalene resembles butyl benzene, $C_6H_5.C_4H_9$, in every particular. The same deportment is noticed with the tetrahydrides of naphthalene derivatives, as well as with those of the naphthylamines (p. 911) and naphthols (p. 916) (Bamberger, *Berichte*, 23, 1124; Ref. 337).

When chlorine is conducted over naphthalene it melts and yields chlorine additive products (p. 581). The *dichloride*, $C_{10}H_8Cl_2$, is a yellow oil, readily decomposing into hydrogen chloride and chlor-naphthalene, $C_{10}H_7Cl$. The *tetrachloride*,

$C_{10}H_8Cl_4$, crystallizes from chloroform in large rhombohedra, melting at 182°. When boiled with alkalies it breaks down into 2HCl and dichlornaphthalene, $C_{10}H_6Cl_2$.

Halogen Derivatives.

α-**Chlor-naphthalene**, $C_{10}H_7Cl$, is produced in chlorinating boiling naphthalene; from naphthalene dichloride (see below) by means of alcoholic potash; from α-naphthalene sulphonic acid with PCl_5, and from α-amido-naphthalene by means of nitrous acid. It is a liquid, boiling about 263°. β-**Chlor-naphthalene**, from β-naphthol and β-naphthylamine, forms pearly leaflets, melts at 61°, and boils at 257°. **Perchlor-naphthalene**, $C_{10}Cl_8$, the final chlorination product, melts about 203°, and boils near 400°.

α-**Brom-naphthalene**, $C_{10}H_7Br$, is produced by bromination; it is a liquid, and boils at 280°. β-**Brom-naphthalene**, from β-naphthylamine and β-naphthol, consists of brilliant leaflets, melting at 68°.

α-**Iodo-naphthalene**, $C_{10}H_7I$, produced by action of iodine upon naphthyl mercury, solidifies only on cooling, and boils about 305°. β-**Iodo-naphthalene**, from β-naphthylamine, melts at 54°.

α-**Fluor naphthalene**, $C_{10}H_7Fl$, from α-naphthylamine, boils at 212°. β-**Fluor-naphthalene** melts at 59°, and boils at 212° (*Berichte*, 22, 1846).

Homologous naphthalenes result from the brom-naphthalenes by the action of alkylogens and sodium, or more easily from naphthalene and alkyl bromides assisted by $AlCl_3$. Methyl naphthalene occurs in slight amounts (*Berichte*, 21, Ref. 355). The methylated naphthalenes are present in coal-tar.

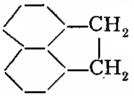
α-**Methyl-naphthalene**, $C_{10}H_7.CH_3$, from α-brom-naphthalene and α-naphthyl-acetic acid (p. 923), is liquid, and boils at 240–242°. β-**Methyl-naphthalene**, from coal-tar, melts at 32°, and boils at 242° (*Berichte*, 17, 842).

Dimethyl-naphthalene, $C_{10}H_6(CH_3)_2$, from dibromnaphthalene and coal-tar, boils at 251°.

α-**Ethyl-naphthalene**, $C_{10}H_7.C_2H_5$, from α-brom-naphthalene, boils near 259°. β-**Ethyl-naphthalene**, from β-brom-naphthalene, and from naphthalene by means of ethyl iodide and aluminium chloride, boils about 250° (*Berichte*, 21, Ref. 356).

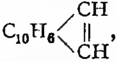
Acenaphthene, $C_{12}H_{10}$, is obtained by conducting α-ethyl naphthalene (or benzene and ethylene) through a red-hot tube, or by the action of alcoholic potash upon α brom-ethyl naphthalene, $C_{10}H_7.C_2H_4Br$ (from α-ethyl naphthalene with bromine at 180°):—

$C_{10}H_7.CH_2.CH_3 =$



$+ H_2$;

this is similar to the formation of naphthalene from phenyl butylene (p. 905). Inasmuch as acenaphthene is oxidized by a chromic acid mixture to naphthalic acid (p. 923) the side-chain C_2H_4 must be arranged in the two peri-positions (1 and 8, p. 907) of naphthalene (*Berichte*, 20, 237 and 657). Consult *Berichte*, 21, 1461, upon nitro- and amido-acenaphthenes.

Acenaphthene occurs in coal-tar, and it separates on cooling from the fraction boiling at 260–280°. It crystallizes from hot alcohol in long needles, melting at 95°, and boiling at 277°. Chromic acid oxidizes it to naphthalic acid, $C_{10}H_6(CO_2H)_2$. It unites with picric acid to form long red needles of $C_{12}H_{10}.C_6H_2(NO_2)_3.OH$, melting at 161°. If the vapors of acenaphthene be passed over ignited plumbic oxide, two hydrogen atoms split off and there results **Acetylene Naphthalene**,  $C_{10}H_6\langle\begin{matrix}CH\\ \|\\ CH\end{matrix}$, acenaphthylene, crystallizing from alcohol in yellow plates, subliming even at the ordinary temperature, melting at 92°, and boiling with partial decomposition at 270°. Its picric acid derivative melts at 202°. Chromic acid oxidizes it to naphthalic acid.

Nitroso-naphthalene, $C_{10}H_7(NO)$, results from the action of nitrosyl bromide upon mercury dinaphthyl in carbon disulphide solution. Ligroïne throws it out of its benzene solution in yellow warts, which redden on exposure. It melts at 89°, decomposes at 134°, possesses a pungent odor, and is readily volatilized in aqueous vapor. It dissolves in sulphuric acid with a cherry-red color. Sulphuric acid imparts a deep-blue color to its solution in phenol (comp. p. 591).

α-Nitro-naphthalene, $C_{10}H_7(NO_2)$, is produced by dissolving naphthalene in glacial acetic acid, adding nitric acid and digesting for about half an hour.

It crystallizes from alcohol in yellow prisms, melts at 61°, and boils at 304°. Chromic acid oxidizes it to α-nitrophthalic acid.

β **Nitronaphthalene**, $C_{10}H_7(NO_2)$, is derived from β-nitronaphthylamine through the diazo-compound. It crystallizes in yellow needles, melting at 79°. It yields β-naphthylamine by reduction (*Berichte*, 20, 891).

Two **Dinitro-naphthalenes**, $C_{10}H_6(NO_2)_2$, are produced when nitronaphthalene is boiled with nitric acid and sulphuric acid. The so-called α-compound (1, 5) consists of colorless prisms, melting at 214°; the β-body crystallizes in rhombic plates, and melts at 170°. The two NO_2-groups occupy the two α-positions and very probably the peri-position (1, 8) (as in acenaphthene and naphthalic acid). A third *γ-dinitronaphthalene* (2, 4) from dinitronaphthylamine (1, 2, 4) melts at 144° (*Berichte*, 20, 973). On boiling the dinitro-naphthalenes with fuming nitric acid, three dinitro- and two tetra-nitronaphthalenes result.

Amido-naphthalenes, $C_{10}H_7.NH_2$.

α-**Amido-naphthalene**,—*α-naphthylamine*, results from the reduction of α-nitronaphthalene, and is obtained on heating α-naphthol with $ZnCl_2$—$CaCl_2$-ammonia (p. 593). It consists of colorless needles or prisms, readily soluble in alcohol, melting at 50°, and boiling at 300°. It acquires a red color on exposure to the air, sublimes readily and possesses a pungent odor. It forms crystalline salts with acids. Oxidizing agents (chromic acid, ferric chloride, silver nitrate) produce a blue precipitate in the solutions of the salts: in a short time this changes into a red powder—oxynaphthamine, $C_{10}H_9NO$. When boiled with chromic acid, naphthylamine yields α-naphthoquinone.

The nitration of the acet-compound (melting at 159°) produces two nitro-compounds; these by saponification with caustic potash change to two *nitronaphthylamines*, $C_{10}H_6(NO_2).NH_2$, α and β (*Berichte*, 19, 796). The *α-compound* (α, α_2 or 1, 4) dissolves with difficulty in alcohol, crystallizes in orange yellow needles, and melts at 191°. It affords α-naphthoquinone upon oxidation; the elimination of its amido-group gives rise to ordinary α-nitronaphthalene. When boiled with potassium hydroxide nitronaphthylamine yields α-nitronaphthol. The β-nitronaphthylamine (αβ or 1, 2) melts at 144°, and when boiled with caustic potash, passes into β-nitronaphthol. Nitrous acid and alcohol convert it into β-nitronaphthalene (*Berichte*, 19, 802).

β-**Amido-naphthalene,** β-*naphthylamine*, is readily obtained by heating β-naphthol with $ZnCl_2$-ammonia to 200° (dinaphthylamine is also produced). It crystallizes from hot water in leaflets, with mother-of-pearl lustre, melts at 112° and boils at 299°. It is odorless. Oxidizing agents do not color it. Potassium permanganate oxidizes it to phthalic acid.

γ-**Nitronaphthylamine,** $C_{10}H_6(NO_2)NH_2$, is produced by nitrating acet-β-naphthylamine and saponifying the product. It melts at 127°, and yields α-nitronaphthalene with nitrous acid and alcohol.

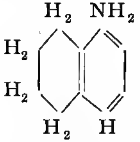
Various dinaphthylamines, $(C_{10}H_7)_2NH$, are obtained upon heating the naphthylamines with zinc chloride or with hydrochloric acid to 179–190°, or with α- and β-naphthols (p. 593). β-Dinaphthylamine, a by-product in the technical preparation of β-naphthylamine, forms leaflets with mother-of-pearl lustre, and melts at 171°. When heated to 150° with concentrated hydrochloric acid it breaks down into β-naphthylamine and β-naphthol. Heated with sulphur it yields **Thio-β-dinaphthylamine,** $C_{10}H_6\left\langle\begin{matrix}NH\\S\end{matrix}\right\rangle C_{10}H_6$, analogous to thiodiphenylamine. **Dinaphthyl-carbazol,** $\left\langle\begin{matrix}C_{10}H_6\\C_{10}H_6\end{matrix}\right\rangle NH$ (p. 847) and **Oxy-dinaphthylamine,** $O\left\langle\begin{matrix}C_{10}H_6\\C_{10}H_6\end{matrix}\right\rangle NH$, are formed when thio-β-dinaphthylamine is heated together with copper (*Berichte*, 19, 2241).

The *phenylnaphthylamines*, $C_{10}H_7.NH.C_6H_5$, result upon heating α- and β-naphthylamine hydrochlorides to 240° together with aniline, or more readily by heating α- and β-naphthol with aniline and zinc chloride. These new compounds combine with diazo salts, forming azo-dyes, which yield *naphthophenazines*, when boiled with acids (*Berichte*, 20, 572).

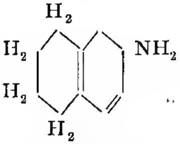
Alkylic anilines are produced analogously to the alkyl anilines by heating the naphthylamine hydrochlorides with alcohols (*Berichte*, 22, 1311).

Hydronaphthylamines.

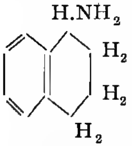
Sodium acting upon the boiling amyl alcohol solution of the naphthylamines causes the latter to add four hydrogen atoms to one of the benzene nuclei. If this addition is made to the non-substituted benzene ring the naphthylamines will continue to show in full degree their aromatic or benzene character; if the opposite should take place, the addition being in the substituted benzene nucleus, the naphthylamines acquire the nature of the amine bases of the paraffin series. The first class of tetrahydro bases have therefore been designated *aromatic* (= *ar*), while the second are called *aliphatic* or *alicylic* (= *al*) (*Berichte*, **22**, 769). The following tetrahydro bases are thus derived from the two naphthylamines (*α*- and *β*):—



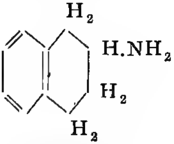
ar-Tetrahydro-α-Naphthylamine.



ar-Tetrahydro-β-Naphthylamine.



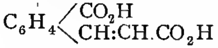
al-Tetrahydro-α-Naphthylamine.



al-Tetrahydro-β-Naphthylamine.

The *aromatic* hydrobases resemble the anilines. They are feeble bases, form salts, having an acid reaction, with acids, are converted into diazo-compounds by nitrous acid, and form azo-dyes by their union with diazo-salts (*Berichte*, **22**, 64). A rather peculiar fact is that they exercise a reducing power with salts of the noble metals. By oxidation all yield adipic acid, $C_4H_8(CO_2H)_2$, owing to the destruction of the unchanged benzene nucleus.

The *alicylic* hydrobases manifest all the properties of the amines. They are strong bases, react alkaline, have an odor like that of piperidine, form neutral salts, do not change to diazo-derivatives under the influence of nitrous acid, but yield very stable nitrites. Potassium permanganate causes the rupture of the hydrogenized benzene ring, and produces *o*-carbon-hydrocinnamic acid,



$$C_6H_4\left\langle\begin{matrix}CO_2H\\CH{:}CH.CO_2H\end{matrix}\right.$$ (p. 791).

ar-**Tetrahydro-*α*-naphthylamine**, from *α*-naphthylamine (see above) (*Berichte*, **21**, 1786, 1892; **22**, 625), is a colorless oil, boiling at 275°. *ar*-**Tetrahydro-*β*-naphthylamine** may be obtained from *β*-naphthylamine, together with the *ac*-compound. It boils at 276°.

ac-**Tetrahydro-*α*-naphthylamine** is prepared by eliminating the NH_2-group from the non-hydrogenized benzene nucleus of tetrahydro-(1, 5)-naphthylenediamine, $C_{10}H_6(H_4)(NH_2)_2$. It is a colorless oil that boils at 246°. Its odor is like that of piperidine. It absorbs carbon dioxide (see above) very energetically (*Berichte*, **22**, 773, 963). *ac*-**Tetrahydro-*β*-naphthylamine** is produced in larger quantities when *β*-naphthylamine is acted upon with metallic sodium. It is perfectly similar to the *ac*-*α*-compound, and boils at 249° (*Berichte*, **21**, 847, 1112).

Perfectly analogous tetrahydrides are derived from the alkylic naphthylamines (*Berichte*, **22**, 772, 1295, 1311). Consult *Berichte*, **22**, 777 upon the physiological action of naphthylamine hydrides.

Diamidonaphthalenes, $C_{10}H_6(NH_2)_2$, *naphthylene diamines*, are obtained by the reduction of dinitro- and nitroamido-naphthalenes, also by the decomposition of amidoazo-naphthalenes, and when dioxynaphthalenes are heated with ammonia (*Berichte*, **21**, Ref. 839; **22**, Ref. 42).

(1, 2) **Naphthylene Diamine** (*αβ*), from *β*-nitro-*α*-naphthylamine and β-naphtho-quinone dioxime (p. 921) (*Berichte*, 19, 179, 803), crystallizes in silvery leaflets from hot water, and melts at 98°. Being an ortho-diamine it can form azine derivatives (*Berichte*, 19, 180, 914).

(1, 3)-**Naphthylene Diamine** is derived from γ-dinitronaphthalene. It is a meta-diamine and hence forms a chrysoïdine with diazobenzene sulphonic acid.

(1, 4)-**Naphthylene Diamine** results from the reduction of α-nitronaphthylamine, and the decomposition of α-amidoazo-naphthalene, by tin and hydrochloric acid. It crystallizes in brilliant scales, and melts at 120°. Ferric chloride converts it into α-naphthoquinone, and bleaching lime changes it to the dichlorimide.

(1, 5)-**Naphthylene Diamine** is prepared from so-called α-dinitronaphthalene (p. 910) and from (1, 5)-dioxynaphthalene. It melts at 189° and then sublimes. Chromic acid does not oxidize it to a naphthoquinone.

(1, 8)-**Naphthylene Diamine**, with the amido-groups in the peri-position (p. 907), is formed by reducing β-dinitronaphthalene. White needles, melting at 66°. Ferric chloride forms a brown precipitate with it. It forms an aldehydine with benzaldehyde. But it differs from the orthodiamines in that it cannot yield a phenazine derivative with phenanthraquinone; this is because it is necessary to have a seven-membered ring (*Berichte*, 22, 861) produced.

The naphthylene diamines resemble the naphthylamines in that they are also able to form *Tetrahydro products*, perfectly analogous to tetrahydronaphthylamines; these possess either an aromatic or alicylic character after the hydrogen addition (*Berichte*, 22, 1374).

(1, 5)-**Tetrahydronaphthylene Diamine**, $C_{10}H_6(H_4)(NH_2)_2$, from (1, 5)-naphthylene diamine, consists of colorless crystals, melting at 77° and boiling at 264°. Its odor is like that of piperidine. It combines at the same time in a remarkable degree (corresponding to the different position of the $2NH_2$-groups) both the aromatic and alicylic character (*Berichte*, 22, 943, 1374). It contains an asymmetric C-atom, therefore may be resolved into a *dextro-* and *lævo-rotatory modification* (Bamberger, *Berichte*, 23, 291). It yields *ac*-α-tetrahydronaphthylamine by the elimination of the amido-group from the non-hydrogenized benzene-ring. This is accomplished through the diazo-compound (see above).

Nitrous acid (or sodium nitrite) acting upon naphthylamine salts produces naphthalene diazo-derivatives, perfectly analogous to the diazobenzene compounds (p. 631); they yield azo-dyes with the anilines and phenols (p. 644).

The **azonaphthalenes**, $C_{10}H_7.N_2.C_{10}H_7$, could not be prepared by reducing nitro napthalenes with alcoholic potash (p. 641).

α-**Azonaphthalene** results upon boiling the diazo-compound $C_{10}H_7.N_2.C_{10}H_6.N_2X$, of α-amidazo-naphthalene with alcohol (p. 632) (*Berichte*, 18, 298, 3252). It crystallizes in red needles, or small steel blue prisms, melting at 190°, and subliming without difficulty. It dissolves with a blue color in concentrated sulphuric acid. This becomes violet at 180°. Boiling alcoholic sodium hydroxide and zinc dust convert it into **Hydrazonaphthalene**, $C_{10}H_7.NH.NH.C_{10}H_7$, which forms colorless leaflets, melting at 275°. The latter compound, when digested with hydrochloric acid, changes to the isomeric **Naphtidine**, $H_2N.C_{10}H_6.C_{10}H_6.NH_2$, diamido-dinaphthyl (compare benzidine, p. 844) (*Berichte*, 18, 3255).

β-Amido-azo-naphthalene (see below) under similar treatment (by means of the diazo-compound) yields β-**Oxyazonaphthalene**, $C_{10}H_7.N_2.C_{10}H_6.OH$ (*Berichte*, 19, 1281). See *Berichte*, 20, 612 for *αβ-azonaphthalene*.

Amido-azonaphthalenes, $C_{10}H_7.N_2.C_{10}H_6.NH_2$.

a-**Amido-azonaphthalene** is formed when nitrous acid acts upon the alcoholic solution of *a*-naphthlyamine; the diazo-amidonaphthalene, $C_{10}H_7.N_2.NH.C_{10}H_7$ (p. 636), first formed undergoes a molecular rearrangement. To prepare it add sodium nitrite (1 molecule) to the aqueous solution of naphthylamine hydrochloride (2 molecules) and neutralize with soda (*Berichte*, 18, 298). It separates in the form of a brown precipitate (see *Berichte*, 22, 590). It crystallizes from alcohol in brownish-red needles or leaflets with green metallic lustre. It melts at 180°. It forms rather unstable yellow-colored salts with one equivalent of the acids. Concentrated acids color the salts dark in the presence of alcohol. Tin and hydrochloric acid resolve *a*-amidoazonaphthalene into *a*-naphthylamine and (1, 4)-naphthylene diamine (p. 913). *Naphthalene Red* belongs to the safranine dyes and is produced when *a*-amidoazonaphthalene is heated with naphthylamine hydrochloride.

β-**Amido-azo-naphthalene**, from *β*-naphthylamine, forms red needles and melts at 156°. It is a very feeble base (*Berichte*, 19, 1282).

*aβ***Amido-azo-naphthalene** results from the action of *a*-naphthylamine upon *β*-naphthylamine diazochloride. It crystallizes in yellowish-brown needles, melting at 152° (*Berichte*, 20, 612).

When diazo salts act upon *β*-naphthylamine products are obtained that manifest the behavior of the diazo-amido, as well as that of the amidazo-derivatives. They are probably *hydrazimido compounds* (p. 640) (*Berichte*, 18, 3132; 20, 1167).

Naphthyl Hydrazines, $C_{10}H_7.NH.NH_2$, are derived from the diazo-chlorides of the two naphthylamines by the action of stannous chloride and hydrochloric acid (p. 653) (*Berichte*, 19, Ref. 303). They crystallize in colorless needles, that readily take on color by exposure to the air. The *a*-compound melts at 117°, the *β*-modification at 125°. They unite with the aldehydes and ketones forming hydrazides; these form naphthindol compounds (p. 923) (*Berichte*, 19, Ref. 831; 22, Ref. 672).

Sulpho-acids.

On digesting four parts of naphthalene with three parts sulphuric acid at 80° we have formed *a*- and *β*-**Naphthalene-sulphonic Acids**, $C_{10}H_7.SO_3H$, which may be separated by means of the barium or lead salts. The free acids are crystalline and deliquesce readily. When heated with sulphuric acid the *a*-acid passes into the *β*-variety (similar to the orthophenol-sulphonic acid); therefore, the latter acid is exclusively produced at higher temperatures (160°). The *a*-acid decomposes upon heating with dilute hydrochloric acid to 200°, into naphthalene and sulphuric acid, whereas the *β*-acid remains unaltered.

Protracted heating of naphthalene with sulphuric acid (5 parts) to 160° produces two **Naphthalene-disulphonic Acids**, $C_{10}H_6(SO_3H)_2$, *a*- and *β*, which can be separated by means of their calcium salts. The *a acid*, containing the two sulpho-groups in two *β*-positions, serves for the preparation of *β*-naphthylamine sulphonic acid (F or *δ*-acid); this possesses technical importance (*Berichte*, 21, 637).

The chief product in sulphonating *a*-nitronaphthalene is (1, 5)-*nitronaphthalene sulphonic acid*, which can also be prepared by the nitration of *a*-naphthalene sulphonic acid. In the latter reaction there is a simultaneous production of (1, 8)-*nitronaphthalene sulphonic acid*, with the peri-position (*Berichte*, 20, 3162; 21, Ref. 730).

Naphthylamine Sulphonic Acids, $C_{10}H_6(NH_2).SO_3H$. There are fourteen isomerides.

(1) The action of sulphuric acid upon α-naphthylamine produces almost exclusively (*Berichte*, **15**, 578; **21**, 2370):—

(1, 4)-**Naphthylamine Sulphonic Acid,** *Naphthionic Acid,* which is applied in the preparation of Congo red.

It crystallizes in small needles, containing one-half molecule of water. At 14° it dissolves in about 4000 parts of water. Its *sodium salt*, $C_{10}H_6(NH_2)SO_3Na + 4H_2O$, crystallizes in large plates or leaflets, which lose their water usually at temperatures above 100°.

(1, 5)-**Naphthylamine Sulphonic Acid**, naphthalidinic acid, is formed by the reduction of (1, 5)-nitronaphthalene sulphonic acid. **Peri-Naphthylamine Sulphonic Acid** (1, 8) is obtained by the reduction of perinitronaphthalene sulphonic acid, and is distinguished from the (1, 4)-acid in that its sodium salt is not very soluble (*Berichte*, **21**, Ref. 730).

The remaining four possible isomeric α-naphthylamine sulphonic acids have also been prepared (*Berichte*, **21**, Ref. 2371).

(2) Four isomeric β-naphthylamine sulphonic acids (designated a, β, γ and δ) have been formed by sulphonating β naphthylamine (*Berichte*, **21**, 637, 3483; **22**, 412, 721). So-called F- or δ *Naphthylamine Sulphonic Acid*, with the two side groups in the two β-positions (2, 6 or 2, 7) has also been obtained from α-naphthalene disulphonic acid (see above), and is especially applied in the preparation of substantive tetrazo-dyes with the benzidines (p. 845) (*Berichte*, **21**, 637).

See *Berichte*, **21**, 3495; **22**, 3327, for the naphthylamine disulphonic acids.

Diazonaphthalene Sulphonic Acid, $C_{10}H_6\left\langle\begin{matrix}SO_2\\N_2\end{matrix}\right\rangle O$, diazonaphthionic acid, is produced by the action of nitrous acid upon naphthionic acid suspended in hot water or alcohol (p. 665). A yellow crystalline powder. It forms rocellin by combining with a naphthol (p. 652).

Naphthol Black is formed by the union of azonaphthalene diazo-sulphonic acid, $C_{10}H_7N_2.C_{10}H_5\left\langle\begin{matrix}N_2\\SO_3\end{matrix}\right\rangle$, with naphthol-monosulphonic acid.

Phenol Derivatives.

In the phenols of naphthalene the hydroxyls are far more reactive than in the benzene phenols. They readily yield amido-naphthalenes with ammonia (p. 593); and upon heating with alcohols and hydrochloric acid naphthol ethers result (*Berichte*, **15**, 1427).

(1) α-**Naphthol**, $C_{10}H_7.OH$, results from α-naphthylamine by means of the diazo-compound, and upon fusing α-naphthalene-sulphonic acid with alkalies. Its formation from phenyl-isocrotonic acid (p. 906) is very noteworthy. It is soluble with difficulty in hot water, readily in alcohol and ether, crystallizes in shining needles; and has the odor of phenol. It melts at 95°, boils at 278–280°, and is readily volatilized. Ferric chloride precipitates violet flakes of dinaphthol, $C_{20}H_{12}(OH_2)$, from its aqueous solution. The *acetate*, $C_{10}H_7.O.C_2H_3O$, melts at 46°; the *ethyl ether*, $C_{10}H_7O.C_2H_5$, boils at 270°.

Metallic sodium converts *a*-napbthol in amyl alcohol solution into

ar-**Tetrahydro-*a*-Naphthol**, $C_{10}H_7(H_4).OH$, which can also be prepared from *ar*-tetrahydro-*a*-naphthylamine by means of the diazo-compound (*Berichte*, 21, 1892). It crystallizes in plates resembling those of naphthalene. It melts at 69° and boils at 265°. It has the character of a true phenol, inasmuch as its hydroxyl is present in the non-hydrogenized benzene ring (*Berichte*, 23, 215).

When the so-called nitroso-*a*-naphthols (p. 920) are oxidized with potassium ferricyanide two **Nitro-*a*-naphthols**, $C_{10}H_6(NO_2).OH$, *a* and *β*, result; these are also obtained when the two nitro-*a*-naphthylamines are boiled with caustic potash (p. 667). The *a-nitro-body* (1, 4) melts at 164°; its sodium salt was applied as *Campo Bello Yellow.* Its reduction gives rise to **Amido-*a*-naphthol**, $C_{10}H_6(NH_2).OH$ (1, 4), which is oxidized to *a*-naphthoquinone by ferric chloride.

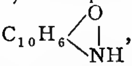
β-**Nitro-*a*-naphthol** (1, 2) is very volatile with steam, and melts at 128° (*Berichte*, 15, 1815).

Dinitro-*a*-naphthol, $C_{10}H_5(NO_2)_2.OH$, is produced by the action of nitric acid upon *a*-naphthol, *a*-naphthol sulphonic acid, upon both nitro-*a*-naphthols, and upon *a*-naphthylamine. It is obtained from the *a*-naphthol sulphonic acid by digestion with common nitric acid. It is almost insoluble in water, sparingly soluble in alcohol and in ether, crystallizes in fine, yellow needles, and melts at 138°. It decomposes alkaline carbonates, and forms yellow salts with one equivalent of base. The salts dye silk a beautiful golden-yellow. The *sodium salt*, $C_{10}H_5(NO_2)_2.ONa + H_2O$, finds use in dyeing, under the name of *naphthalene yellow* (Martius yellow). The *potassium salt* of dinitronaphthol-sulphonic acid, $C_{10}H_4(NO_2)_2\left\{\begin{matrix}SO_3K\\OK\end{matrix}\right.$, obtained by the nitration of naphthol-trisulphonic acid, is *naphthol yellow.*

Further nitration of dinitronaphthol with nitric-sulphuric acid produces **Trinitronaphthol**, $C_{10}H_4(NO_2)_3.OH$, which crystallizes from glacial acetic acid in yellow needles or leaflets, melting at 177°. Its salts show the same color as naphthalene yellow.

(1, 4)-Amido-*a*-naphthol, $C_{10}H_6(NH_2).OH$, results from the reduction of (1, 4)-nitronaphthol, and by the decomposition of *a*-naphthol orange, $C_{10}H_6(OH).N_2.C_6H_4.SO_3H$ (from *a*-naphthol and diazo-benzene sulphonic acid). It is very unstable even in the form of a salt. It yields *a*-napthoquinone by oxidation.

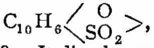
(1, 2)-Amido-*a*-naphthol, from (1, 2)-nitronaphthol, oxidizes in the air to *a*-naphthoquinonimide, $C_{10}H_6(NH)O$, or



$C_{10}H_6\left\langle\begin{matrix}O\\|\\NH\end{matrix}\right.$, forming violet leaflets (*Berichte*, 18, 572). Chromic acid oxidizes it to *β*-naphthoquinone. **(1, 5)-Amido-*a*-naphthol** is formed when naphthylamine sulphonic acid (p. 914) is heated with alkalies. It combines with naphthalene diazosulphonic acid to form a dye with a blue color (*Berichte*, 23, Ref. 41).

***a*-Naphthol Sulphonic Acids**, $C_{10}H_6(OH).SO_3H$.

Two acids (*a*- and *β*-) are produced when *a*-naphthol is digested with concentrated sulphuric acid (2 parts.) The *a-acid* (Schaeffer) has the position (1, 2); ferric chloride imparts a deep blue color to it. The *β-acid* is (1, 4) and is derived from naphthionic acid (p. 915) (*Berichte*, 22, 996; 21, Ref. 731). **(1, 5)-Naphthol Sulphonic Acid** may be obtained from naphthylamine sulphonic acid. **Perinaphthol Sulphonic Acid** (1, 8) is formed from peri-naphthylamine sulphonic acid by decomposing its diazo-derivative with water. It then separates as a lactone-like **anhydride**,



$C_{10}H_6\left\langle\begin{matrix}O\\SO_2\end{matrix}\right\rangle$, **naphsulphtone.** This consists of shining prisms, melting at 154°. It dissolves with difficulty in water and alcohol. It shows neutral reaction. It dissolves in the hot alkalies, forming salts of perinaphthol sulphonic acid; when the latter is liberated it dissolves quite easily in water, and is colored dark green and then red by ferric chloride (*Berichte*, 21, Ref. 731). See *Berichte*, 23, 3088, upon the *a*-naphthol-disulphonic acids.

2. β-**Naphthol**, $C_{10}H_7.OH$, from β-naphthalene-sulphonic acid and β-naphthylamine, is readily soluble in hot water, crystallizes in leaflets, melting at 122°, and boiling at 286°, and is very volatile. Ferric chloride imparts a greenish color to the solution and separates dinaphthol, $C_{20}H_{12}(OH)_2$, melting at 216°. The *acetate* melts at 61°.

Metallic sodium acting upon the amyl alcohol solution of β-naphthol produces both aromatic and alicylic tetrahydronaphthols (just as β-naphthylamine yields the two tetrahydrides, p. 912) (*Berichte*, 23, 197, 1127).

ar-**Tetrahydro-β-naphthol**, $C_{10}H_{11}.OH$, forms silvery white needles, melting at 58° and boiling at 275°. Its odor is like that of phenol, and in its entire deportment it resembles the benzene phenols (*Berichte*, 23, 885, 1129).

ac-**Tetrahydro-β-naphthol** is a viscid oil, with an odor like that of sage. It boils at 264°. It differs from the phenols in being insoluble in alkalies, its character corresponds to that of the paraffin alcohols, and it closely resembles borneol and menthol, which possess a similar constitution (*Berichte*, 23, 204).

By the oxidation of so called *a*-nitroso-β-naphthol (p. 920), we obtain *a*-**Nitro-β-naphthol**, $C_{10}H_6(NO_2).OH$, which is also formed from nitro-β-naphthylamine, when it is boiled with sodium hydroxide. It consists of brown leaflets, melting at 103°. **Dinitro-β-naphthol**, $C_{10}H_5(NO_2)_2.OH$, is obtained by the nitration of β-naphthol in alcoholic solution, and also from β-naphthylamine (*Berichte*, 17, 1171). It melts at 195° (*Berichte*, 23, 2542).

Amido-β-naphthol, $C_{10}H_6(NH_2).OH$ (1, 2), is obtained in the reduction of nitro-β-naphthol (1, 2) with tin and hydrochloric acid; also from β-naphthol orange (see below) or from benzene azo-β-naphthol by decomposition with tin and hydrochloric acid (*Berichte*, 16, 2861). Its hydrochloride crystallizes in white needles; it yields β-naphthoquinone when oxidized.

On the addition of alcoholic β-naphthol to the solution of diazo-benzene-sulphonic acid we get β-**Naphthol-azo-benzene-sulphonic Acid**, $C_{10}H_6(OH).N_2.C_6H_4.SO_3H$, whose sodium salt is the *β-Naphthol-orange—Mandarin*. The diazo-group occupies the ortho-place referred to hydroxyl (p. 644); tin and hydrochloric acid decompose the azosulphonic acid into amido-β-naphthol (1, 2) and sulphanilic acid. By the conjugation of diazo-naphthalene sulphonic acid (p. 915) and β-naphthol (above), β-**Naphthol-azo-naphthalene-sulphonic Acid**, $C_{10}H_6(OH).N_2.C_{10}H_6.SO_3H$, is produced. Its sodium salt, the so-called *Pure red* or *Rocellin*, is used as a substitute for archil and cochineal. The *Bieberich scarlets* are formed by the conjugation of β-naphthol with diazo-azobenzene-sulphonic acids.

β-**Naphthol Sulphonic Acids**, $C_{10}H_6(OH).SO_3H$.

Four of the seven possible isomerides are known. They are applied in the preparation of colors (*Berichte*, 21, 3473).

When β-naphthol is dissolved in concentrated sulphuric acid at the ordinary temperature the first product is β naphthyl sulphonic acid, $C_{10}H_7.O.SO_3H$. By continuous digestion this is almost entirely changed to **β-naphthol-β-sulphonic acid** (Schäffer's sulpho-acid) (probably 2, 6) (*Berichte*, 18, Ref. 89). β-**Naph-**

thol-α-sulphonic acid (Baeyer's Acid or Croceïn Acid) (2, 5) or (2, 8) (formerly thought to be 2, 1) is produced at the same time (*Berichte*, 21, 3489; 22, 396, 453). It serves for the preparation of croceïn scarlet.

The (2, 7)-**β-Naphthol Sulphonic Acid** (Cassella's Acid, or F-acid) is produced when α-naphthalene disulphonic acid is fused with caustic soda at 200–250°. The (2, 5)-**Naphthol Sulphonic Acid** (of Dahl) is made by diazotizing β-naphthylamine-γ-sulphonic acid. Four **Amido-Naphthol-Sulphonic Acids,** $C_{10}H_5(NH_2)(OH).SO_3H$, have been obtained from the azo dyes, formed by the reduction of the products resulting from the union of these four β-naphthol acids with diazo-derivatives. Two β-naphthol disulphonic acids, $C_{10}H_5(OH)(SO_3H)_2$, called R- and G-acid, are produced when β-naphthol is digested with sulphuric acid (4 parts) at 100°. They form various *Ponceaus* by conjugation with xylidines and cumidines. The G-acid, obtained in perfectly pure condition from β-naphthol-α-sulphonic acid (see above), is known in commerce as **β-Naphthol-γ-Disulphonic Acid**; it yields especially valuable dyestuffs (*Berichte*, 21, 3478). See *Berichte*, 22, 822; 23, 3045, for **Thionaphthols.**

Dioxynaphthalenes, $C_{10}H_6(OH)_2$. Six of the ten possible isomerides are known; of these we mention those corresponding to the two naphthoquinones.

α-**Hydronaphthoquinone** (1, 4) is obtained from α-naphthoquinone on boiling with hydriodic acid and phosphorus. It crystallizes from hot water in long needles, and melts at 173°. Chromic acid readily oxidizes it to α-naphthoquinone.

β-**Hydronaphthoquinone** (1, 2) separates in silvery leaflets, melting at 60°, when a solution of β-naphthoquinone in aqueous sulphurous acid stands for some time. It dissolves in the alkalies with a yellow color which becomes an intense green upon exposure.

(1, 5)-**Dioxynaphthalene** is derived from α-nitronaphthalene sulphonic acid and by fusing γ-naphthalene disulphonic acid with caustic potash. It readily sublimes in thin leaflets and melts at 186°. Chromic acid oxidizes it to juglone (p. 919). (2, 7)-**Dioxynaphthalene** is obtained from α-naphthalene disulphonic acid, crystallizes in long needles and melts at 190° (*Berichte*, 23, 519).

Trioxynaphthalenes, $C_{10}H_5(OH)_3$.

Two trioxynaphthalenes, α- and β-**Hydrojuglones,** occur in green walnut shells (*Berichte*, 18, 463, 2567). α-**Hydrojuglone** (1, 5) crystallizes in needles or leaflets, melting at 169°. In the air it rapidly oxidizes to juglone (see below). If it be distilled it changes to β-**Hydrojuglone,** which dissolves in water with more difficulty and does not yield juglone upon oxidation. It reverts again to α-hydrojuglone when boiled with dilute alcoholic hydrochloric acid. The two hydrojuglones yield the same triacetyl compound with acetic anhydride.

Quinones.

In addition to ordinary α-naphthoquinone, corresponding in all respects to benzoquinone, there is a β-naphthoquinone, which represents an ortho-diketone (compare *o*-benzoquinone, p. 704).

(1) α-**Naphthoquinone,** $C_{10}H_6O_2$ (1, 4), is formed in the oxidation of α-naphthylamine, nitro-α-naphthol, diamidonaphthalene

(1, 4), and amido-α-naphthol (1, 4) with chromic acid; further, on heating naphthalene in glacial acetic acid with chromic acid (p. 699, *Berichte*, **20**, 2283). It crystallizes from hot alcohol in yellow rhombic plates, melting at 125° and subliming under 100°. It possesses the usual quinone odor, is very volatile, and distils over in a current of steam. Nitric acid oxidizes it to phthalic acid, and by reduction forms α-naphthohydroquinone (see above).

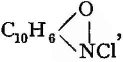
ar-**Tetrahydro-α-naphthoquinone**, $C_{10}H_6(H_4)O_2$, is produced by the oxidation of *ar*-tetrahydro-α-naphthylamine (p. 912) with chromic acid. Its pronounced benzene character harmonizes with its constitution. It resembles benzoquinone more closely than α-naphthoquinone. It melts at 55°, but is incapable of forming a hydrazone (*Berichte*, 23, 1131). α-Naphthoquinone and phenylhydrazine combine to *hydrazones* (distinction from ordinary benzoquinone). The *dioxime* is derived from the *monoxime* by means of hydroxylamine. The *Anilide*, $C_{10}H_5(NH.C_6H_5)O_2$ (p. 700), results from the union of α-naphthoquinone with aniline. It crystallizes in red needles, that melt at 191°. Boiling dilute sodium hydroxide decomposes it into aniline and β-oxy-α-naphthoquinone, $C_{10}H_5(O_2)$.OH (1, 4, 2), naphthalene acid, that melts at 188°.

Juglone is an α-oxy-α-naphthoquinone, $C_{10}H_5(O_2)$.OH (1, 4—5 or 8). The best method to obtain it consists in oxidizing α-hydrojuglone with ferric chloride. It may be synthetically prepared by oxidizing (1, 5)-dioxynaphthalene with chromic acid (*Berichte*, 20, 934). It is almost insoluble in water, consists of yellow needles and melts with decomposition about 150–155°. It dissolves in alkalies with a violet color. Zinc dust converts it into naphthalene. Nitric acid converts it into dinitro-oxyphthalic acid (juglonic acid) (*Berichte*, 19, 164).

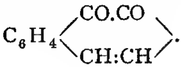
The following are *dioxy-a-naphthoquinones*, $C_{10}H_4(OH)_2O$:—

Oxy-juglone, formed by the oxidation of the alkaline solution of juglone on exposure to the air. Golden yellow plates, that melt at 220°, with decomposition.

Naphthalizarin, corresponding to the alizarin of anthracene, is derived from α-dinitronaphthalene by heating it with concentrated sulphuric acid and zinc. It sublimes in red needles with green metallic reflex, dissolves in ammonia with a bright blue color, and yields violet-colored precipitates with lime or baryta water.

α-**Naphthoquinone Chlorimide**,  $C_{10}H_6\left\langle\begin{array}{l}O\\ |\\ NCl\end{array}\right.$, obtained from amido-$\alpha$-naphthol hydrochloride with a solution of bleaching lime (p. 705), consists of brown needles, melting at 85°. It yields *a-Naphthol-blue* (p. 707), with dimethyl aniline.

(2) β-**Naphthoquinone**, $C_{10}H_6O_2$ (1, 2), is produced on oxidizing amido-β-naphthol with chromic acid or with ferric chloride (*Berichte*, 17, Ref. 531). It also results from the decomposition of β-naphthol orange (p. 917) and further oxidation with ferric chloride (*Berichte*, **21**, 3472). It crystallizes from ether or benzene in orange-colored leaflets, and decomposes at 115–120°. It is distinguished from the real quinones (p. 698), by being odorless and non-volatile. It closely resembles anthraquinone, and especially phenanthraquinone (p. 925); like the latter it must be considered an ortho-diketone :—

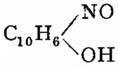


$$C_6H_4\left\langle\begin{array}{l}CO.CO\\ CH{:}CH\end{array}\right\rangle.$$

In accordance with this view it combines with one and two molecules of $H_2N.OH$, yielding quinoximes.

Phenylhydrazine unites with it forming the *hydrazone*, $C_{10}H_6O(N_2H.C_6H_5)$ (p. 921), melting at 138°. Sulphurous acid reduces it at ordinary temperatures to β-naphtho-hydroquinone. Potassium permanganate oxidizes it to phthalic acid.

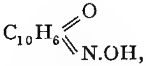
Naphthoquinoximes or Nitrosonaphthols. These are produced when the alcoholic solutions of the naphthoquinones are boiled with hydroxylamine hydrochloride, and by the action of nitrous acid upon the naphthols. Their constitution corresponds to the formulas:—



$$C_{10}H_6\begin{cases} NO \\ OH \end{cases}$$

Nitrosonaphthol.

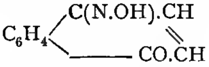
or



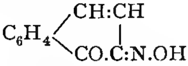
$$C_{10}H_6\begin{cases} {=}O \\ {=}N.OH, \end{cases}$$

Quinoxime.

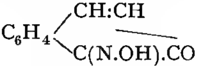
which are probably tautomeric (pp. 674, 699). Three isomerides are produced according to the preceding methods:—



α-Nitroso-α-naphthol.
α-Naphthoquinoxime.



β-Nitroso-α-naphthol.
β-Naphthoquinoxime.



α-Nitroso-β-naphthol.

Nitrous acid acting upon α-naphthol produces both α- and β-nitroso-α-naphthol (Preparation, *Berichte*, 18, 706). The first may be obtained from α-naphthoquinone by means of hydroxylamine (*Berichte*, 17, 2064). Nitrous acid converts β-naphthol into but one compound *α-nitroso-β-naphthol* (Preparation, *Berichte*, 18, 705), whereas β-nitroso-α-naphthol is the product if hydroxylamine be used (*Berichte*, 17, 215). The three compounds behave like feeble acids; they dissolve in alkaline carbonates, and are again liberated by carbon dioxide. They form corresponding nitronaphthols upon oxidation.

α-Nitroso-α-naphthol or *α-naphthoquinoxime* consists of colorless needles, melting at 190°. *β-Nitroso-α-naphthol* (β-naphthoquinoxime) crystallizes in needles from hot water, and melts at 152°. *α-Nitroso-β-Naphthol* forms stout yellow-brown prisms, melts at 160°, and volatilizes with aqueous vapor (*Berichte*, 17, 2584). It precipitates various metals from solutions of their salts, and may be employed in separating cobalt from nickel (*Berichte*, 18, 699), iron from aluminium (*Berichte*, 18, 2728), and for the determination of copper and iron (*Berichte*, 20, 283).

The *methyl ethers* of β-nitroso-α-naphthol and of α-nitroso-β-naphthol, $C_{10}H_6(N.O.CH_3)O$ (derived from the silver salts with methyl iodide), are reduced to amidonaphthols by tin chloride (*Berichte*, 18, 571). The behavior of the two compounds toward hydroxylamine hydrochloride argues in favor of their being quinoximes (*Berichte*, 19, 341). The same conclusion is deduced from the behavior of α- and β naphthoquinones toward methyl hydroxylamine $H_2N.O.CH_3$ (*Berichte*, 18, 2225).

α-**Naphthoquinone Dioxime,** $C_{10}H_6\begin{cases} {=}N.OH \\ {=}N.OH, \end{cases}$ is formed upon boiling α nitroso-α-naphthol with hydroxylamine hydrochloride and aqueous alcohol. It crystallizes in colorless needles and melts at 207°. Acetic anhydride converts it into a diacetate (*Berichte*, 21, 433).

β-Naphthoquinone Dioxime, $C_{10}H_6{<}\begin{matrix}N.OH\\ N.OH\end{matrix}$ (Di-isonitroso-naphthalene hydride), is derived from β-nitroso-α-naphthol, and from α-nitroso-β-naphthol by the action of hydroxylamine hydrochloride (*Berichte*, 17, 2064, 2582). It crystallizes from water in yellow needles and melts at 149°. It forms the *anhydride*, $C_{10}H_6\left\{\begin{matrix}N\\ N\end{matrix}\right\rangle O$, melting at 78°, when digested with alkalies. Stannous chloride reduces the dioxime to (1, 2)-naphthylenediamine. β-Naphthoquinone dioxime colors iron and cobalt mordants brown. The same may be said of other ortho-dioxime and ortho-oxy-oxime (1, 2) dye-substances, but not of the para-dioximes (*Berichte*, 22, 1349).

Quinone Phenylhydrazones.

Phenylhydrazine hydrochloride acting upon α-naphthoquinone in glacial acetic acid produces *α-naphthoquinone phenylhydrazone*, identical with *Benzene-azo-naphthol* derived from α-naphthol and diazobenzene chloride. The two formulas,

$$C_{10}H_6{<}\begin{matrix}O & (1)\\ N.NH.C_6H_5 & (4\end{matrix}$$

and

$$C_{10}H_6{<}\begin{matrix}OH\\ N{:}N.C_6H_5\end{matrix}$$

are probably, therefore, tautomeric, and the compound reacts at the same time as a phenol and a base (*Berichte*, 17, 3026). However, *β-naphtho-quinone phenylhydrazone* differs from benzene-azo β naphthol, $C_{10}H_6\left\{\begin{matrix}O\\ N_2\dot{H}.C_6H_6\end{matrix}\right.$ (*Berichte*, 18, 796; 21, 414). The toluenes exhibit a similar deportment (*Berichte*, 19, 2486).

Alcohols, Ketones, Nitriles.

α-**Naphthobenzyl Alcohol,** $C_{10}H_7.CH_2OH$, from α-naphthobenzylamine (from α-naphthonitrile, see below), crystallizes in long, brilliant needles, melts at 60° and boils at 301° (*Berichte*, 21, 257). Chromic acid oxidizes it to

α-**Naphthaldehyde,** $C_{10}H_7.CHO$, a thick oil, boiling at 291° (*Berichte* 22, 2148).

β-**Naphthaldehyde,** $C_{10}H_7.CHO$, is produced by the distillation of the calcium salts of β-naphthoic and formic acids, and by the oxidation of β-naphthyl carbinol, $C_{10}H_7.CH_2.OH$ (from β-cyan naphthalene). It crystallizes from hot water in shining leaflets, that melt at 59° (*Berichte*, 16, 636; 20, 1115).

Dinaphthyl Ketones, $C_{10}H_7.CO.C_{10}H_7$, α- and β-, result by the condensation of α- and β-naphthoic acids with naphthalene upon heating them with phosphorus pentoxide, also by the action of naphthalene and zinc upon α- and β-naphthoyl chloride, $C_{10}H_7.COCl$ (p. 855).

α-**Naphthyl-methyl Ketone,** $C_{10}H_7.CO.CH_3$, is derived from naphthalene and acetyl chloride by means of aluminium chloride. It melts at 34° and boils about 295°. It unites with hydroxylamine and phenylhydrazine. Potassium permanganate oxidizes it to naphthyl glyoxylic acid (p. 923).

The corresponding cyanides or nitriles may be obtained by the distillation of the alkali salts of the naphthalene-disulphonic acids, or the phosphoric esters of the naphthols with potassium cyanide (*Berichte*, 21, Ref. 834).

α-**Cyan-naphthalene,** $C_{10}H_7.CN$, has also been prepared from naphthyl formamide, $C_{10}H_7.NH.COH$ (from naphthylamine oxalate) (comp. p. 633) as well as from α-naphthalene diazochloride by means of copper and potassium cyanides (*Berichte*, 20, 241). It dissolves readily in alcohol, and forms flat needles, melting at 37.5°, and distilling at 298°. **β-Cyan-naphthalene**, from β-naphthalene sulphonic acid, crystallizes in yellow prisms, melts at 61°, and distils at 304°.

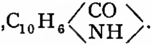
Similarly, two **naphthalene-dicyanides**, $C_{10}H_6(CN)_2$, are produced from the two naphthalene disulphonic acids. Both sublime in shining needles; the α-compound melts at 268° and is almost insoluble in the ordinary solvents; the β-dicyanide dissolves in hot alcohol, and melts at 297°.

Naphthalene carboxylic acids are produced on saponifying the cyan-naphthalenes with alcoholic potassium hydroxide.

Naphthalene Carboxylic Acids.

α-Naphthoic Acid, $C_{10}H_7.CO_2H$, from α-cyan-naphthalene, by saponification with alcoholic soda at 160° (*Berichte*, **20**, 242; **21**, Ref. 834), is also prepared by fusing potassium α-naphthalene sulphonate with sodium formate, and by the action of sodium amalgam on a mixture of α-brom-naphthalene and chlor-carbonic ester. It consists of fine needles, melting at 160°, and dissolving in hot water with difficulty, but readily in hot alcohol.

The nitration of α-naphthoic acid produces two nitro-naphthoic acids, $C_{10}H_6(NO_2).CO_2H$. *α-Nitronaphthoic Acid* (1, 5) is almost totally insoluble in hot water. It forms delicate needles and melts at 239°. Potassium permanganate oxidizes it to α-nitrophthalic acid; boiling nitric acid converts it into α-dinitro-naphthalene. Ferrous sulphate and ammonia reduce it to a stable *amido-naphthoic acid* (1, 5), melting at 212° (*Berichte*, **19**, 1981).

β-Nitronaphthoic Acid (1, 8) contains the two side groups in the peri-position. It consists of hard prisms and melts at 275°. Boiling nitric acid converts it into (1, 8)-dinitronaphthalene. Ferrous sulphate and ammonia reduce it to (1, 8)-*amidonaphthoic acid*, which when free passes quite readily into its inner anhydride, **Naphthostyril**,  $C_{10}H_6\left\langle\begin{matrix}CO\\NH\end{matrix}\right\rangle$. The latter forms yellowish-brown needles, melting at 179° (*Berichte*, **19**, 1131). Naphthalic acid is produced by the rearrangement of the amido-acid through the diazo-compound into cyan-naphthoic acid etc. (*Berichte*, **20**, 240).

β-Naphthoic Acid, $C_{10}H_7.CO_2H$, from β-cyan-naphthalene, crystallizes from hot water in long, silky needles, and melts at 182°. Baryta converts it (as well as α-naphthoic acid) into naphthalene and carbon dioxide.

Oxy-naphthoic Acids, $C_{10}H_6(OH).CO_2H$. Naphthol carboxylic acids. Eight of the fourteen possible isomerides are known.

α-Naphthol Carboxylic Acid (1, 2) corresponds to salicylic acid. It is produced in an analogous manner from α-naphthol, best by heating the sodium salt with CO_2 under pressure (p. 768). It dissolves with difficulty in hot water, crystallizes in needles and melts at 186°. Ferric chloride imparts an intense blue color to it (*Berichte*, **21**, 1186).

β-Naphthol Carboxylic Acid (2, 1—OH in 2) is derived from β-naphthol-sodium with carbon dioxide and pressure at 120–145° (*Berichte*, **20**, 2701), as well as by carefully fusing β-naphthol aldehyde, $C_{10}H_6(OH).CHO$, with caustic potash (*Berichte*, 15, 805). It crystallizes from dilute alcohol in needles, is colored violet by ferric chloride, melts at 156° when rapidly heated and decomposes into CO_2 and naphthol. It sustains an analogous decomposition when it is boiled with water.

If β-naphthol-sodium be heated more strongly, 200–250°—in a current of carbon dioxide the product will be an isomeric *naphthol carboxylic acid*. This is colored yellow and melts at 216° (*Berichte*, 23, Ref. 612).

(1, 8)-Naphthol Carboxylic Acid is derived from (1, 8)-amido-naphthoic acid (see above) by means of the diazo-compound. It melts at 109° and breaks down into water and its *γ-lactone*, $C_{10}H_6{<}\begin{smallmatrix}O\\CO\end{smallmatrix}{>}$, melting at 169°.

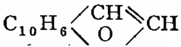
α-Naphthyl-glyoxylic Acid, Naphthoyl Formic Acid, $C_{10}H_7.CO.CO_2H$, obtained from α-naphthoyl chloride by means of the cyanide (p. 762), and from α-naphthyl methyl ketone by oxidation with permanganate, melts at 113°, and yields **α-naphthyl acetic acid,** $C_{10}H_7.CH_2.CO_2H$, when reduced; this melts at 131°.

Naphthalene Dicarboxylic Acids, $C_{10}H_6(CO_2H)_2$. Six of the ten possible isomerides are known. When acenaphthene and ace-naphthylene are oxidized with chromic acid we get **Naphthalic Acid** (1, 8), which contains the carboxyl groups in the peri-position. It crystallizes in small needles, which decompose at 140–150°, without melting, into water, and its anhydride, $C_{10}H_6(CO)_2O$, that crystallizes from alcohol in needles, and melts at 266°. It is perfectly analogous to phthalic anhydride (*Berichte*, 20, 240).

Tetrahydro-naphthalene Dicarboxylic Acid, $C_{10}H_{10}{<}\begin{smallmatrix}CO_2H\\CO_2H\end{smallmatrix}$ (β, β), obtained by saponifying the ethyl ester of the tetracarboxylic acid (p. 906), melts at 199° and decomposes into water and its anhydride, that melts at 184°.

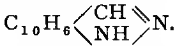
Naphthalene Tetracarboxylic Acid, $C_{10}H_4(CO_2H)_4$ (1, 8–4, 5), with the carboxyl groups in the two peri-positions of naphthalene, results when pyrenic acid is carefully oxidized by potassium permanganate (*Berichte*, 20, 365). It forms shining needles and yields naphthalene upon distillation with lime.

Derivatives of **Naphtho-furfurane** and **Naphthindol** (p. 825).



$C_{10}H_6{<}\begin{smallmatrix}CH\\O\end{smallmatrix}{>}CH$

Naphtho-furfurane.



$C_{10}H_6{<}\begin{smallmatrix}CH\\NH\end{smallmatrix}{>}N.$

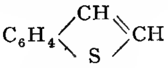
Naphthopyrrol.

The naphthofurfurane derivatives (α and β) are derived, analogously to the benzofurfurane compounds, by the action of sodium α- and β-naphthol upon chloracetoacetic ester (p. 817). One derivative is formed from each, whereas according to the naphthalene formula two (1, 2) and (1, 8), and (2, 1) and (2, 3) isomerides are possible with each. The first products are methyl-naphtho-furfurane carboxylic esters, $C_{10}H_6{:}C_2O(CH_3).CO_2R$; by saponification these yield the free acids, from which by loss of carbon dioxide are obtained the **methyl naphtho-furfuranes,** $C_{10}H_6{:}C_2HO(CH_3)$ (*Berichte*, 19, 1301).

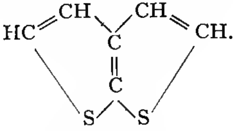
The naphthindol or naphthopyrrol derivatives, like the indol derivatives, are prepared from the compounds of α- and β-naphthylhydrazines with aldehydes, ketones and ketonic acids, when they are heated together with zinc chloride (*Berichte*, 19, Ref. 831; 20, Ref. 428). **α-Naphthindol,** $C_{10}H_6{:}C_2H_3N$, crystallizes in leaflets and melts at 175°. **β-Naphthindol** is a liquid and boils above 360°.

See *Berichte*, 21, 114, for β-**Naphthoxindol** and β-**Naphthisatin.**

Thionaphthene and **Thiophtene** bear the same relation to naphthalene that thiophene bears to benzene:—


Thionaphthene.

and


Thiophtene.

Thionaphthene, C_8H_6S, has already been given as benzothiophene (p. 826).

Thiophtene, $C_6H_4S_2$, consisting of two condensed thiophene nuclei, is produced when citric acid is heated with P_2S_5 (p. 529). It is an oil, boiling at 225°. (*Berichte*, 19, 2444).

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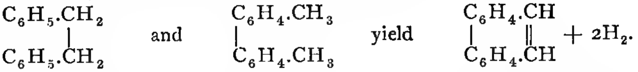
2. PHENANTHRENE GROUP.

Phenanthrene, $C_{14}H_{10}$ (p. 905), occurs in coal-tar and in the so-called "stubb," a mass of substance obtained (together with fluoranthene) in the distillation of mercury ores in Idria. It is prepared synthetically (with diphenyl, anthracene and other hydrocarbons) from various benzene compounds, by conducting their vapors through a red-hot tube, *e. g.*, from toluene, stilbene, diphenyl and ethylene, from dibenzyl and ortho-ditolyl:—



$$\begin{matrix} C_6H_5.CH_2 \\ | \\ C_6H_5.CH_2 \end{matrix} \quad \text{and} \quad \begin{matrix} C_6H_4.CH_3 \\ | \\ C_6H_4.CH_3 \end{matrix} \quad \text{yield} \quad \begin{matrix} C_6H_4.CH \\ | \quad\ \ \| \\ C_6H_4.CH \end{matrix} + 2H_2.$$

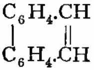
Dibenzyl. o-Ditolyl. Phenanthrene.

Sodium acting on ortho-brom benzylbromide, $C_6H_4Br.CH_2.Br$, also produces it (together with anthracene, p. 893). It also appears in the condensation of coumarone with benzene upon the application of heat (*Berichte*, 23, 85).

Phenanthrene is obtained from crude anthracene by taking that fraction boiling at 320–350°, concentrating it by further distillation, and crystallizing from alcohol, when anthracene will separate first. The phenanthrene is obtained from its picric acid compound, or by oxidation with chromic acid, when the anthracene will be first attacked (*Annalen*, 196, 34; *Berichte*, 19, 761).

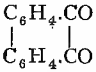
Phenanthrene crystallizes in colorless, shining leaflets or plates, melting at 99°, boiling at 340°, and subliming readily. It dissolves in 50 parts of alcohol at 14°, and in 10 parts (95 per cent.) on boiling, and readily in ether and benzene. The solutions exhibit a blue fluorescence. The picric acid compound, $C_{14}H_{10}.C_6H_2(NO_2)_3.OH$, separates in yellow needles on mixing the alcoholic solutions, and melts at 144°. Phenanthrene is oxidized by boiling with chromic acid to phenanthraquinone, then to diphenic acid.

Phenanthrene must, from its formation from dibenzyl and ortho-brombenzyl bromide, be considered a diphenyl derivative, in which two ortho-places of the two benzene nuclei are united by the group C_2H_2; the latter, therefore, forms, with the four carbon atoms of the two benzene rings, a third normal benzene ring. So-called phenanthraquinone, the oxidation product of phenanthrene, must be regarded as an ortho-diketone (p. 699), because further oxidation converts it into diphenic acid (p. 849), in which the two carboxyl groups are inserted in two ortho-places of diphenyl:—



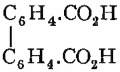
$$\begin{array}{l} C_6H_4.CH \\ |\qquad\ \| \\ C_6H_4.CH \end{array}$$

Phenanthrene.



$$\begin{array}{l} C_6H_4.CO \\ |\qquad\ | \\ C_6H_4.CO \end{array}$$

Phenanthraquinone.



$$\begin{array}{l} C_6H_4.CO_2H \\ | \\ C_6H_4.CO_2H \end{array}$$

Diphenic Acid.

Hydrogen additive products result upon heating phenanthrene with hydriodic acid and phosphorus. The *tetra-hydride*, $C_{14}H_{14}$, boils at 310°, and solidifies on cooling. The *Per-hydride*, $C_{14}H_{24}$, melts at −3° and boils at 270–275° (*Berichte*, 22, 779). Chlorine produces substitution products, of which the *octo-chloride*, $C_{14}H_2Cl_8$, melts at 270–280°, and by further chlorination (comp. p. 580) is split into hexachlorbenzene, C_6Cl_6, and CCl_4. Bromine combines with phenanthrene in CS_2 solution, yielding the *dibromide*, $C_{14}H_{10}.Br_2$, which melts at 98°, with decomposition, and readily breaks up into hydrogen bromide and *bromphenanthrene*, $C_{14}H_9Br$. This melts at 63°, and is oxidized to phenanthraquinone by chromic acid.

Ordinary nitric acid converts phenanthrene into three *nitrophenanthrenes*, $C_{14}H_9(NO_2)$, which yield three *amido-phenanthrenes*, $C_{14}H_9(NH_2)$, by reduction. Two *phenanthrene-sulphonic acids*, $C_{14}H_9.SO_3H$, are produced on digesting phenanthrene with sulphuric acid. If these be distilled with yellow prussiate of potash we obtain two *cyanides*, $C_{14}H_9.CN$, yielding the corresponding carboxylic acids.

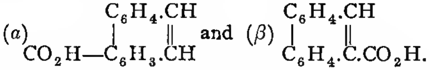
Phenanthraquinone, $C_{14}H_8O_2$, an ortho-diketone (see above), is formed in the action of chromic acid upon phenanthrene in glacial acetic acid solution; most readily by heating it with a chromic acid mixture (*Annalen*, **196**, 38). It crystallizes from alcohol in long, orange-yellow needles, melts at 198°, and distils without decomposition. It is not very soluble in hot water or cold alcohol, but readily in hot alcohol, ether and benzene. It dissolves in concentrated sulphuric acid with a dark green color, and is reprecipitated by water. By adding toluene containing thiotolene and sulphuric acid to the acetic acid solution of phenanthraquinone a bluish-green coloration is produced (p. 572).

Like β-naphthoquinone phenanthraquinone is odorless, not volatile in steam, and is readily reduced by sulphurous acid. Like the latter, too, it unites with one and two molecules of $H_2N.OH$. The **monoxime**, $C_{14}H_8O(N.OH)$, consists of golden yellow needles, melting at 158°, and dissolving with a red color in sulphuric acid. If it is heated together with glacial acetic acid and hydrochloric acid to 130° it sustains the transposition of ketoximes (p. 727), and forms **diphenimide**, $C_{12}H_8\left\langle\begin{smallmatrix}CO\\CO\end{smallmatrix}\right\rangle NH$ (*Berichte*, 22, Ref. 591). The *dioxime* forms an anhydride, $C_{14}H_8\left\langle\begin{smallmatrix}N\\N\end{smallmatrix}\right\rangle O$, melting at 181°. An isomeric monoxime or dioxime has not been prepared (p. 727) (*Berichte*, 22, 1985).

Phenanthraquinone forms phenazine derivatives with ortho-diamines. Being a ketone it also combines with primary sodium sulphite to form the crystalline derivative, $C_{14}H_8O_2.SO_3HNa + 2H_2O$, from which it is again separated by alkalies or acids. By oxidation with chromic acid, or by boiling with alcoholic potash, phenanthraquinone is oxidized to diphenic acid; ignition with soda-lime produces diphenylene ketone (p. 851), fluorene and diphenyl. Diphenylene glycollic acid (p. 851), fluorene alcohol and diphenylene ketone are obtained on boiling with aqueous soda-lye. Ignited with zinc dust we obtain phenanthrene.

On digesting phenanthraquinone with concentrated sulphurous acid it changes to **Dioxyphenanthrene**, $C_{14}H_8(OH)_2$ (phenanthrene hydroquinone), which crystallizes from hot water in colorless needles that turn brown on exposure, and reoxidize to phenanthraquinone. The *diacetate* crystallizes from benzene in plates, melting at 202°.

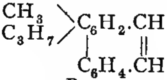
By saponifying the two phenanthrene cyanides we obtain two **Phenanthrenecarboxylic Acids**, $C_{15}H_{10}O_2$:—



$$(\alpha)\ \begin{array}{r} C_6H_4.CH \\ | \qquad \| \\ CO_2H—C_6H_3.CH \end{array} \quad \text{and} \quad (\beta)\ \begin{array}{l} C_6H_4.CH \\ | \qquad \| \\ C_6H_4.C.CO_2H. \end{array}$$

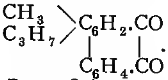
The α-acid melts at 266°, and is oxidized to phenanthraquinone carboxylic acid, $C_{14}H_7(O_2)CO_2H$, by chromic acid; the β-acid melts at 251°, and yields phenanthraquinone.

Retene, $C_{18}H_{18}$, is a derivative of phenanthrene. It represents a methyl isopropyl phenanthrene (*Berichte*, 18, 1027; Ref. 558):—



$$\left.\begin{array}{r} CH_3 \\ C_3H_7 \end{array}\right\rangle \begin{array}{l} C_6H_2.CH \\ | \qquad \| \\ C_6H_4.CH \end{array}$$

Retene.



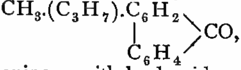
$$\left.\begin{array}{r} CH_3 \\ C_3H_7 \end{array}\right\rangle \begin{array}{l} C_6H_2.CO \\ | \qquad | \\ C_6H_4.CO \end{array}.$$

Retene Quinone.

Retene occurs in the tar of highly resinous pines, and in some mineral resins. It is isolated from those portions that boil at elevated temperatures. It is very soluble in alcohol and benzene. It crystallizes in leaflets with mother-of-pearl lustre, melts at 98°, and boils about 390°. It is very volatile in steam. Its picric acid compound forms orange-yellow needles, melting at 123°. Chromic acid in glacial acetic acid solution oxidizes retene to **retene quinone**, $C_{18}H_{16}O_2$ (see above)—a red powder, crystallizing in orange-red needles that melt at 197°. It dissolves in caustic potash with a dark-red color; this disappears upon shaking in contact with air. It yields retene by the distillation with zinc dust. It resembles phenanthraquinone in its entire deportment. It is an orthodiketone. Sulphurous acid reduces it on application of heat to **Retene Hydroquinone**, $C_{18}H_6(OH)_2$;

air reoxidizes it to retene quinone. Hydroxylamine converts it into a quinone oxime, $C_{18}H_{16}O(N.OH)$, and quinone dioxime, $C_{18}H_{16}(N.OH)_2$, golden yellow leaflets, that melt at 129°. It forms retene phenazine, $C_{18}H_{16}\left(\begin{matrix}N\\N\end{matrix}\!>\!C_6H_4\right)$ (p. 629) with *o*-phenylenediamine.

Sodium hydroxide converts retene quinone into two rather unstable acids—**Retene Diphenic Acid,** $C_{16}H_{16}\langle\begin{matrix}CO_2H\\CO_2H\end{matrix}$, and **Retene Glycollic Acid,** $C_{16}H_{16}.CH(OH).CO_2H$ (see p. 851). Potassium permanganate oxidizes retene quinone to diphenylene ketone dicarboxylic acid (p. 852) and retene ketone,



$\begin{matrix}CH_3.(C_3H_7).C_6H_2\\|\\C_6H_4\end{matrix}\!\!>\!CO$, which can be more easily prepared by distilling retene quinone with lead oxide. When the latter is distilled with zinc dust the product is retene fluorene, $C_{17}H_{18}$ (p. 851). Pearly leaflets, melting at 97° (*Berichte*, 18, 1754).

Retene Dodecahydride, $C_{18}H_{30}$, a blue fluorescent oil, boiling at 336° (*Berichte*, 22, 780), is formed when retene is heated with hydriodic acid and phosphorus to 250°. It is identical with dehydrofichtelite.

Fichtelite, $C_{18}H_{82}$, occurs together with retene in the peat of fossil pines. It crystallizes from ligroïne and alcohol in vitreous prisms. It melts at 46° (*Berichte*, 22, 498, 635). When heated to 150° with iodine it loses two hydrogen atoms and forms **Dehydrofichtelite,** $C_{18}H_{30}$, identical with retene dodecahydride. Fichtelite is, therefore, retene perhydride, $C_{16}H_{32}$ (*Berichte*, 22, 3369).

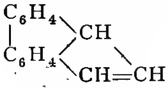
Besides the hydrocarbons with high boiling points which have been derived from coal-tar and already described; naphthalene, $C_{10}H_8$ (B. P. 218°); methyl-naphthalene, $C_{11}H_{10}$ (240°); acenaphthene, $C_{12}H_{10}$ (278°); fluorene, $C_{13}H_{20}$ (305°); phenanthrene, $C_{14}H_{10}$ (340°), and anthracene, $C_{14}H_{10}$ (360°), we have the following: fluoranthene, $C_{15}H_{10}$, pyrene, $C_{16}H_{10}$, and chrysene, $C_{18}H_{12}$. These have been isolated from the so-called crude phenanthrene, the fraction boiling above 360°.

Fluoranthene and pyrene occur chiefly in the first fractions. They are separated by fractional distillation under diminished pressure; fluoranthene boiling at 250° under 60 mm. pressure; pyrene at 260°. Their perfect separation is then effected by the fractional crystallization of their picric acid derivatives (*Annalen*, 200, 1). The portions boiling at the most elevated temperatures consist mainly of pyrene and chrysene, which are separated by means of carbon disulphide (which dissolves pyrene) and by the crystallization of their picric acid combinations (*Annalen*, 158, 285 and 299).

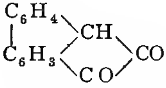
Pyrene and fluoranthene (idryl) also occur in the "stubb-fat" obtained from the distillation of the "stubb" (p. 924).

Fluoranthene, $C_{15}H_{10}$, **Idryl,** crystallizes from alcohol in needles or plates, melting at 109–110°, and dissolves readily in hot alcohol, ether and carbon disulphide. It dissolves with a blue color in warm sulphuric acid. Its *picric acid compound*, $C_{15}H_{10}.C_6H_2(NO_2)_3OH$, consists of reddish-yellow needles, is sparingly soluble in ether, and melts at 182°. Fuming nitric acid converts idryl into the trinitro-compound, $C_{15}H_7(NO_2)_3$, melting above 300°. **Fluoranthraquinone,** $C_{15}H_8O_2$, is obtained by oxidizing idryl with chromic acid. It crystallizes from alcohol in small, red needles, melting at 188°, and dissolves, like phenanthrene, in alkaline bisulphites. If the quinone be further oxidized (with elimination of CO_2) we obtain diphenylene-ketone carboxylic acid.

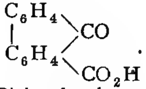
The constitution of fluoranthene and of fluoranthoquinone probably corresponds to the formulas (*Annalen*, 200, 20): —



Fluoranthene.



Fluoranthoquinone.



Diphenylene-ketone Carboxylic Acid.

Pyrene, $C_{16}H_{10}$, is sparingly soluble in hot alcohol (33 parts), readily in ether, benzene and carbon disulphide, crystallizes in colorless leaflets or plates, and melts at 148°. The picric acid compound crystallizes from alcohol in long needles, and melts at 222°. Chromic acid oxidizes it to **Pyrenquinone**, $C_{16}H_8O_2$, a brick-red powder, which is almost completely decomposed when heated.

Pyrenic Acid, $C_{15}H_8O_5$, results upon further oxidation of pyrenquinone. It is an ortho-dicarboxylic acid. It forms an anhydride or imide compound quite readily. It consists of golden yellow leaflets, and at 120° breaks down into water and its anhydride. Being a ketone it combines with one molecule of phenylhydrazine (*Berichte*, 19, 1997). When pyrenic acid is distilled with lime, it forms **Pyrene Ketone**, $C_{12}H_8(CO)$, crystallizing in yellow plates that melt at 141°. Being a ketone, it combines with phenylhydrazine and sodium bisulphite. Potassium permanganate oxidizes pyrenic acid to naphthalene tetracarboxylic acid (p. 923), and pyrene ketone to naphthalic acid, which yields naphthalene upon distillation with lime.

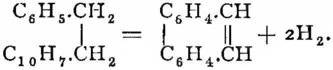
Pyrene is, therefore, very probably a naphthalene, in which both peri-positions (1, 8 and 4, 5) are replaced by two groups, CH.CH.CH, so that four symmetrical condensed benzene nuclei are produced (*Berichte*, 20, 365; *Annalen*, 240, 147).

Chrysene, $C_{18}H_{12}$ (p. 927), is generally colored yellow (hence the name), but can be rendered perfectly colorless by the action of different reagents. It is very sparingly soluble in alcohol, ether and carbon disulphide, and rather readily soluble in hot benzene and glacial acetic acid; it melts at 250°, and boils at 436°. It crystallizes and sublimes in silvery leaflets, which exhibit an intense violet fluorescence. The picric acid compound crystallizes from hot benzene in red needles, and is decomposed by alcohol. When digested with chromic acid and glacial acetic acid it oxidizes to so-called **Chrysoquinone**, $C_{18}H_{10}O_2$ (a diketone), which crystallizes in red needles, melting at 235°, and dissolving in sulphuric acid with a blue color; water reprecipitates chrysoquinone. It unites as a ketone with primary sodium sulphite. Sulphurous acid reduces it to the hydroquinone, $C_{18}H_{10}(OH)_2$.

Chrysoketone, $C_{17}H_{10}O$ (compare retene ketone), results when chrysoquinone is distilled with lead oxide. It crystallizes in bright red colored needles, melting at 132°. Hydriodic acid and phosphorus, upon application of heat, reduce it to chrysofluorene, $C_{17}H_{12}$ (melting at 187°).

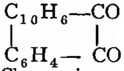
Chrysenic Acid, $C_{17}H_{12}O_3$ (phenylnaphthyl carboxylic acid), is produced when chrysene is fused with caustic alkali. It forms silver-white leaflets and melts at 186°. When it is dissolved in sulphuric acid it reverts to chrysoketone (*Berichte*, 23, 2440).

Chrysene is prepared synthetically from benzyl-naphthyl-ketone, $C_6H_5.CH_2.CO.C_{10}H_7$ (from phenyl acetic chloride, $C_6H_5.CH_2.COCl$, and naphthalene with $AlCl_3$), if the latter be converted by heating with hydriodic acid and phosphorus into the hydrocarbon, $C_6H_5.CH_2.CH_2.C_{10}H_7$, and then distilling this through a red-hot tube—just as phenanthrene is produced from dibenzyl:—



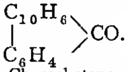
$$\begin{array}{r}C_6H_5.CH_2\\ |\\ C_{10}H_7.CH_2\end{array} = \begin{array}{l}C_6H_4.CH\\ |\qquad\ \|\\ C_6H_4.CH\end{array} + 2H_2.$$

Chrysene is similarly formed by heating naphthalene with coumarone, $C_6H_4\left<\begin{matrix}CH\\O\end{matrix}\right>CH_2$—just as phenanthrene is obtained from coumarone and benzene (p. 924) (*Berichte*, 23, 84). Therefore, chrysene consists, in all probability, of four unsymmetrical, condensed benzene nuclei; and chrysoquinone and chrysoketone would then have the following formulas (see *Berichte*, 23, 2433):—



$$\begin{matrix}C_{10}H_6—CO\\ | \qquad\quad |\\ C_6H_4—CO\end{matrix}$$

Chrysoquinone.

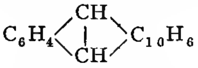


$$\begin{matrix}C_{10}H_6\\ | \\ C_6H_4\end{matrix}>CO.$$

Chrysoketone.

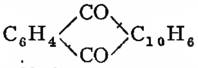
The liquid *hydride*, $C_{18}H_{28}$, boiling about 360°, is produced when chrysene is heated together with hydriodic acid and phosphorus. A later product is **Chrysene Perhydride,** $C_{18}H_{30}$, crystallizing in white needles, melting at 115° and boiling about 353° (*Berichte*, 22, 135).

Naphanthracene, $C_{16}H_{12}$, from naphanthraquinone, $C_{16}H_{10}O_2$, on digesting it with zinc dust and ammonia, is isomeric with chrysene. It is produced by the condensation of naphtoyl-*o*-benzoic acid (from phthalic anhydride with naphthalene and $AlCl_3$ p. 863) upon heating it with sulphuric acid, just as anthraquinone is derived from *o*-benzoyl-benzoic acid (p. 893) (*Berichte*, 19, 2209):



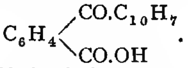
$$C_6H_4\left<\begin{matrix}CH\\ | \\CH\end{matrix}\right>C_{10}H_6$$

Naphanthracene.



$$C_6H_4\left<\begin{matrix}CO\\CO\end{matrix}\right>C_{10}H_6$$

Naphanthraquinone.



$$C_6H_4\left<\begin{matrix}CO.C_{10}H_7\\CO.OH\end{matrix}\right..$$

Naphtoyl-*o*-benzoic acid.

Naphanthracene crystallizes from alcohol in colorless leaves, having a strong greenish-yellow fluorescence. It melts at 141° and sublimes. It combines with two molecules of picric acid, $C_{18}H_{12}.2C_6H_3(NO_2)_3O$, forming red needles melting at 133°. **Naphanthraquinone,** $C_{18}H_{10}O_2$ (see above), crystallizes and sublimes in yellow needles or leaflets and melts at 168°. It dissolves with a brown color in concentrated sulphuric acid; water reprecipitates it unchanged.

Picene, $C_{22}H_{14}$, is a hydrocarbon formed by the distillation of lignite, coal-tar and petroleum residues. It is very sparingly soluble in most of the solvents, but most readily in crude cumene, crystallizes in blue fluorescent leaflets, melting at 338°, and boils at 519°. It dissolves with a green color in sulphuric acid and is oxidized by chromic acid to an orange-red *quinone*, $C_{22}H_{12}O_2$. When heated to 250° with hydriodic acid and phosphorus **Picene Perhydride,** $C_{22}H_{36}$, is produced. It forms white needles melting at 175° and boiling above 360° (*Berichte*, 22, 781).

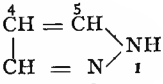
DERIVATIVES OF NUCLEI CONTAINING NITROGEN.

A. Derivatives of five-membered nuclei containing nitrogen.

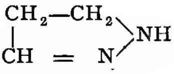
The five-membered parent nuclei and their derivatives were almost entirely disposed of before the aromatic compounds were taken up. Mention must, however, be made of the phenylated diazoles: of *pyrazole* and of *glyoxaline* (p. 551).

1. PHENYLATED PYRAZOLES.

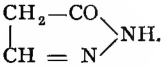
The parent nuclei of the derivatives belonging to this class are:—



Pyrazole.



Pyrazoline.



5-Pyrazolon.

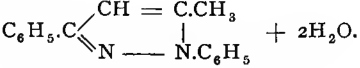
The positions of substituting groups in these parent nuclei are designated by the numbers 1–5, corresponding to the notation of the pyrazole nucleus. Pyrazoline and pyrazolidine (p. 551) bear the same relation to pyrazole as pyrroline and pyrrolidine to pyrrol (p. 549). The nucleus of *pyrazolon* or *ketopyrazoline*, containing oxygen, corresponds to pyrrolidon and the pyridine and lutidine of the pyridine group (p. 944). The term *5-pyrazolon* serves to distinguish this from the possible 3- and 4-pyrazolons, in which the oxygen occupies positions 3 and 4.

The pyrazole compounds (formerly called quinazine derivatives) were discovered by L. Knorr in 1883 (*Berichte*, **16**, 2597; *Annalen*, **238**, 137). *Antipyrine* belongs to this group. It has great technical value.

1. *Pyrazole-derivatives*, in which oxygen is not present, are produced:—

(1) By heating the β diketones,*—CO.CHR.CO—of the benzene and paraffin series with primary phenylhydrazines. The immediate products are the phenylhydrazones (p. 656); these eliminate water and a closed ring results. Thus, benzoyl acetone (p. 731) and phenylhydrazine yield **Diphenylmethyl Pyrazole** (*Berichte*, **18**, 2135):—

$$C_6H_5.CO.CH_2.CO.CH_3 + H_2N.HN.C_6H_5 =$$



(1, 3, 5)-Diphenyl-methyl Pyrazole.

In like manner we obtain (1, 3, 5)-*phenyl dimethyl pyrazole*, from acetyl acetone, $CH_3.CO.CH_2.CO.CH_3$ (*Berichte*, **20**, 1104); and *benzyl phenyl methyl-pyrazole* (*Berichte*, **18**, 2137) from phenylacetyl acetone, $C_6H_5.CH_2.CO.CH_2.CO.CH_3$ (p. 731). (1, 3, 5)-*Triphenyl pyrazole* is derived from dibenzoyl methane, $C_6H_5.CO.CH_2.CO.C_6H_5$ (p. 891) (*Berichte*, **21**, 1206).

Pyrazole carboxylic esters are formed in an analogous manner from β-diketone carboxylic esters. For example, benzoyl aceto-acetic ester (p. 816) and phenyl hydrazine yield (1, 3, 5)-*diphenyl methyl-pyrazole-4-carboxylic ester* (*Berichte*, **18**, 311):—

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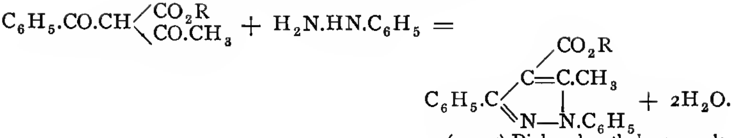
* The γ-diketones combine with the phenylhydrazines, forming pyridazine compounds (p. 954), whereas the derivatives of the α-diketones with two molecules of phenylhydrazine remain unchanged.



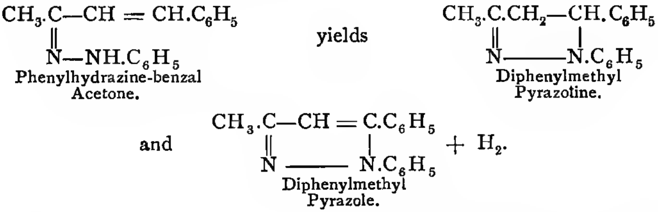
(1, 3, 5)-Diphenyl-methyl-4-pyrazole Carboxylic Acid.

The corresponding nitro-derivatives (*Berichte*, **18**, 2256) are similarly formed from *o*- and *p*-nitro-benzoyl aceto-acetic ester. The free acid results upon saponifying the ester; when it loses carbon dioxide it passes into (1, 3, 5)-diphenyl-methyl-pyrazole (see above) (*Berichte*, **20**, 1096). Under like treatment acetyl aceto-acetic ester, $CH_3.CO.CH(CO.CH_3).CO_2R$, furnishes (1, 3, 5)-phenyldimethyl pyrazole-4-carboxylic ester, from which by saponification and elimination of carbon dioxide, it is possible to obtain (1, 3, 5)-phenyldimethyl pyrazole, $C_3HN_2(C_6H_6)(CH_3)_2$ (*Berichte*, **20**, 1101). Further, benzoyl pyroracemic ester $C_6H_6.CO.CH_2.CO.CO_2H$ (p. 765), becomes diphenylpyrazole-carboxylic ester, which then yields (1, 3)-diphenyl pyrazole, $C_3H_2N_2(C_6H_5)_2$ (*Berichte*, **20**, 2185).

2. The β- or (1, 3)-ketone aldehydes react like the β-diketones. Thus we obtain from acetylaldehyde, $CH_3.CO.CH_2CHO$, (1, 5)-*phenyl methyl pyrazole*, from propionyl aldehyde, $CH_3.CH_2.CO.CH_2.CHO$, *phenyl ethyl pyrazole* (*Berichte*, **21**, 1147), from propionyl propionic aldehyde, $CH_3.CH_2.CO.CH(CH_3).CHO$, *phenylmethylethyl pyrazole* (*Berichte*, **22**, 3276), and from benzoyl aldehyde, $C_6H_5.CO.CH_2.CHO$ (p. 730), (1, 5)-*diphenylpyrazole* (*Berichte*, **21**, 1138), etc.

Epichlorhydrin conducts itself in a similar manner with the formation of 1-*phenyl-pyrazole*, which may also be prepared from phenyl pyrazole tricarboxylic acid (*Berichte*, **22**, 180, Ref. 238, 554). It is a yellow oil; when it has been solidified it remelts at 11° and boils at 246°.

3. From the *unsaturated* ketones and aldehydes, CHR:CR.COR and CHR:CR.COH, when they are heated with the phenylhydrazines. The phenylhydrazine formed at first loses, when distilled, two hydrogen atoms, and yields the corresponding *pyrazole* derivative; the *pyrazoline* compound, isomeric with the latter, is formed simultaneously by mere molecular re-arrangement of the phenyl-hydrazone (*Annalen*, **238**, 141; *Berichte*, **20**, 1097). In this way benzal acetone, $CH_3.CO.CH:CH.C_6H_5$ (p. 805) and phenylhydrazine form (1, 5, 3)-*diphenylmethyl pyrazole* and *pyrazoline* (*Berichte*, **20**, 1100):—



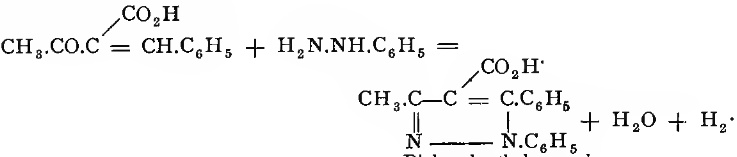
Phenylhydrazine-benzal Acetone.

Diphenylmethyl Pyrazoline.

Diphenylmethyl Pyrazole.

The latter is isomeric with (1, 3, 5)-diphenylmethyl pyrazole. Under similar treatment ethidene acetone, $CH_3.CO.CH:CH.CH_3$ (p. 195), yields *phenyl dimethyl-pyrazoline* (*Berichte*, **22**, 1105). Cinnamic aldehyde forms (1, 5)-*diphenylpyrazoline*, and (1, 3, 5)-*triphenylpyrazoline* is obtained from benzalacetophenone, $C_6H_5.CH:CH.CO.C_6H_5$ (*Berichte*, **21**, 1201).

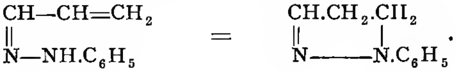
Pyrazole carboxylic esters are similarly derived from *unsaturated* ketone carboxylic acids (their esters); the pyrazoles can be prepared from these. Thus, benzal aceto-acetic ester and phenylhydrazine yield (1, 5, 3)-*diphenyl methyl pyrazole-4-carboxylic-ester* :—



Diphenylmethyl-pyrazole
Carboxylic Ester.

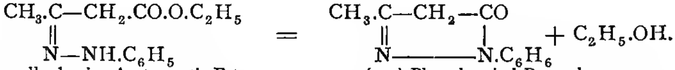
(1, 5, 3)-Diphenylmethyl-pyrazole (see above) results upon saponifying the ester and eliminating carbon dioxide (*Annalen*, 238, 139). Ethidene aceto acetic ester yields (1, 3, 5)-phenyldimethyl-4-carboxylic ester; when this is saponified and loses carbon dioxide it forms (1, 3, 5)-phenyldimethyl-pyrazole (*Berichte*, 22, 1101).

The unsaturated aldehydes react very much like the unsaturated ketones. Acroleïn-phenylhydrazide yields 1-*phenyl pyrazoline* (*Annalen*, 239, 195) :—



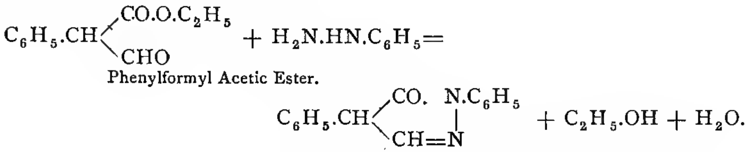
The *phenyl pyrazoles* are feeble bases; water readily decomposes their salts; they volatilize with steam from acid solutions. Nitrous acid does not affect them. Sodium, acting upon their alcoholic solution, converts them into the corresponding *pyrazolines*. The latter are also weak bases; oxidizing agents (nitrous acid, chromic acid and ferric chloride) convert them into fuchsine red dyes—*pyrazole* reaction of Knorr (*Annalen*, 238, 200).

2. The oxygen-containing *pyrazolon*-derivatives (see above) are produced, if β-ketonic acids, $R.CO.CH_2.CO_2H$, be substituted for β-diketones in the formation of the phenylpyrazoles, or if, instead of unsaturated ketones, aldehydes and ketone carboxylic acids, unsaturated acids be allowed to react with phenylhydrazines. Acetoacetic ester and phenylhydrazine condense to a hydrazone, which, upon being heated, splits off alcohol and forms (1, 3)-*phenyl-methyl pyrazolon* (*Annalen*, 238, 146) :—



Phenylhydrazine Aceto-acetic Ester. (1, 3)-Phenylmethyl Pyrazolon.

(1, 3)-Diphenylpyrazolon is similarly formed from benzoyl acetic ester, $C_6H_5.CO.CH_2.CO_2.C_2H_5$ (*Berichte*, 20, 2545; 21, Ref. 201). The phenylhydrazide of unsaturated phenylacrylic acid, $C_6H_6.CH:CH.CO.NH.NH.C_6H_5$, when distilled, loses two hydrogen atoms and forms (1, 5)-Diphenylpyrazolon, $C_{15}H_{14}N_2O = C_{15}H_{12}N_2O + H_2$ (*Berichte*, 20, 1107). Oxalylacetic ester (p. 435) (*Berichte*, 19, 3227) and succino-succinic ester (p. 795) (*Berichte*, 17, 2053) react analogously. The ester of phenylformyl acetic acid (a β-aldehydic acid) reacts similarly to the esters of β-ketonic acids with the formation of (1, 4)-diphenylpyrazolon (*Berichte*, 20, 2933):—



$$C_6H_5.CH\begin{array}{l}\diagup CO.O.C_2H_5\\ \diagdown CHO\end{array} + H_2N.HN.C_6H_5 =$$

Phenylformyl Acetic Ester.

$$C_6H_5.CH\begin{array}{l}\diagup CO.\ \ N.C_6H_5\\ \qquad\quad\ |\\ \diagdown CH{=}N\end{array} + C_2H_5.OH + H_2O.$$

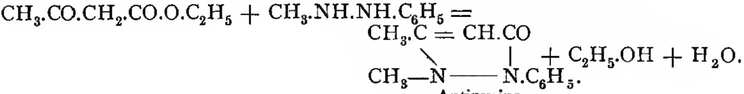
(1, 4)-Diphenyl pyrazolon.

As the CH_2-group of the pyrazolon compounds, obtained from acetyl- and benzoyl-acetic esters, is retained unaltered, all mono- and di-substituted acetoacetic acid esters (*e.g.*, methyl- and dimethyl-acetoacetic ester, acetosuccinic ester, etc.), are capable of yielding pyrazolon compounds with primary phenylhydrazines. On the other hand, the unsymmetrical β-compounds (not the α-derivatives, p. 657), from the alkylic phenylhydrazines, are able to form derivatives of the isopyrazolon nucleus (antipyrine compounds). Tolylhydrazine, naphthylhydrazine, etc., react in the same manner as phenylhydrazine (*Berichte*, 17, 549). Hydrazobenzene, $C_6H_5.NH.NH.C_6H_5$, reacts just the same as the β-alkyl phenylhydrazines (p. 649).

(1, 3)-**Phenylmethyl Pyrazolon**, $C_3H_2O(CH_3)N_2(C_6H_5 = C_{10}H_{10}N_2O$, resulting from acetoacetic ester and phenylhydrazine (*Annalen*, **238**, 147), crystallizes from hot water in prisms, melting at 127° and boiling at 287°. It manifests the feeble basic character of the pyrazole bases, and at the same time the acid nature of acetoacetic ether. It is soluble in acids and alkalies. The hydrogen of its CH_2-group will answer all the reactions of the same group in aceto-acetic ester; it can be replaced by metals, alkyls, etc. Ferric chloride or platinic chloride oxidizes the pyrazolon to *pyrazole blue* (see below). This reaction serves for the recognition of all pyrazolon compounds containing the CH_2-group intact.

When (1,-3)-phenylmethyl pyrazolon is heated to 100° with methyl iodide and methyl alcohol, it sustains a partial transposition and forms

Phenyldimethyl Pyrazolon, $C_{11}H_{12}N_2O = C_3H(CH_3)_2N_2(C_6H_5)O$ (1, 2, 3), *Antipyrine*. This is derived from the unaltered isopyrazolon nucleus (with a different arrangement of the hydrogen atoms), and may be directly synthesized by heating acetoacetic ester with α-methyl-phenyl-hydrazine, $C_6H_5.NH.OH.CH_3$ (see below) (*Annalen*, **238**, 160, 203; *Berichte*, **20**, Ref. 609):—

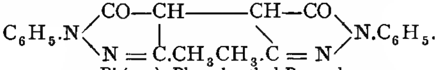


$$CH_3.CO.CH_2.CO.O.C_2H_5 + CH_3.NH.NH.C_6H_5 = \begin{array}{l}CH_3.C = CH.CO\\ \quad\ \diagdown \qquad\quad |\\ CH_3{-}N{-\!-\!-}N.C_6H_5.\end{array} + C_2H_5.OH + H_2O.$$

Antipyrine.

Antipyrine, rather singularly, is very soluble in water, alcohol and chloroform. It crystallizes from ether and toluene in shining leaflets, melting at 113°. It is a strong monacid base, that forms salts with ease. Ferric chloride colors its aqueous solution red, and nitrous acid imparts a bluish-green color to it (*Annalen*, 238, 203). It is used as an antipyretic.

Many derivatives are obtained by the substitution of the hydrogen of the CH_2 group in phenylmethylpyrazolon. Compounds like benzylidene-phenylmethylpyrazolon are formed upon heating it together with aldehydes. These are red dye-substances. They correspond to the indogenides of pseudoindoxyl (p. 833). *Bi-phenylmethyl Pyrazolon* is formed by moderated oxidation or by the action of iodine upon silver phenylmethyl pyrazolon. It can also be obtained synthetically from diaceto-succinic ester, and two molecules of phenylhydrazine. *Pyrazole Blue* (*Annalen*, 238, 171) is even formed in the cold by further oxidation with ferric chloride, etc.:—



Bi-(1, 3)- Phenylmethyl Pyrazolon.

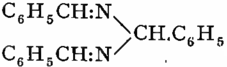
Pyrazole Blue.

Pyrazole blue results directly upon boiling phenylmethylpyrazolon with ferric chloride. In properties and constitution it is very similar to indigo blue.

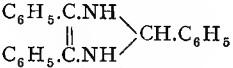
Phenylmethyl pyrazolon exhibits great similarity also to barbituric acid (malonyl urea, p. 441). Its isonitroso-, nitro- and amido-derivatives correspond perfectly to violuric acid, dilituric acid, and the uramile of the uric acid group. When the amido group is oxidized *rubazonic acid* is produced; this corresponds to purpuric acid (*Annalen*, 238, 192). Rubazonic acid and phenylhydrazine unite to a *hydrazone*, that is identical with an *azo-compound* derived from phenylmethyl pyrazolon and benzene diazochloride (*Berichte*, 21, 1201).

2. PHENYLATED GLYOXALINES (p. 929).

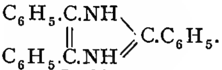
The alkyl glyoxalines have been discussed. The phenylated glyoxalines will be here considered. **Lophine**, $C_{21}H_{16}N_2$, and **Amarine**, $C_{12}H_{18}N_2$, belong in this class. They are triphenyl derivatives of glyoxaline and dihydroglyoxaline, and bear a close relation to hydrobenzamide (p. 717) and triphenyl-cyanide, $(C_6H_5.CN)_3$ (*Berichte*, 18, 1849, 3085):—



Hydrobenzamide.



Amarine.

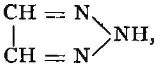


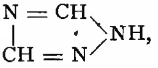
Lophine.

Triphenyl Glyoxaline, $C_3N_2H(C_6H_5)_3$, *Lophine*, is produced when amarine or hydrobenzamide is subjected to distillation, or if the former be oxidized with chromic acid (in glacial acetic acid), or from cyanphenine, $(C_6H_5.CN)_3$, by the action of nascent hydrogen (with disengagement of NH_3). It may be prepared synthetically by acting with ammonia upon an alcoholic solution of benzil, with benzaldehyde, in the same manner as glyoxalethylins are obtained from glyoxal with aldehydes (p. 552). Lophine is not readily soluble in alcohol, crystallizes in long needles, and melts at 275°. It yields crystalline salts with one equivalent of the acids. It exhibits the property of phosphorescing in marked degree when shaken with alcoholic potash; it is then decomposed into ammonia and benzoic acid (p. 189). Like the glyoxalines, it does not form an acetate.

Triphenyl Dihydroglyoxaline, $C_3N_2H_3(C_6H_5)_3$, *Amarine*, results from a rearrangement of the isomeric hydrobenzamide, caused by boiling it with caustic potash or upon heating it to 130°. It crystallizes from alcohol and ether in prisms, melting at 113°. It reacts (in alcoholic solution) alkaline, and with one equivalent of the acids yields salts which are sparingly soluble in water. Amarine affords dialkyl derivatives when it is heated with alkyl iodides, whereas only mono-alkyl compounds result with lophine.

3. PHENYLATED TRIAZOLES (p. 553).

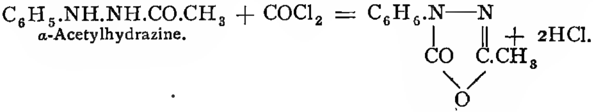

Osotriazone.


Triazole.

Triphenyl Osotriazone, $C_2N_3(C_6H_5)_3$, from benzil dihydrazone, consists of pearly leaflets, melting at 122° (*Berichte*, **21**, 2806).

The diketo derivatives of **Tetrahydrotriazole**, $C_2N_3H_7$, have been called *urazoles* (p. 553).

In conclusion, mention must be made of the *biazole ring*. Its phenyl derivatives, formerly termed **phenyl carbizines**,  and considered such, result in the action of phosgene gas upon the *a-acid* or urea-derivatives of the phenylhydrazines (*Berichte*, **21**, 2456; **23**, 2843):—



Phenylmethyl Biazolon.

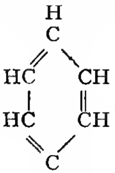
Phenyl Biazolon, $C_6H_5.C_2N_2O_2H$, is analogously formed from formyl phenylhydrazine (p. 658), and was formerly designated formylphenyl carbizine. It melts at 73° and boils at 255°. **Phenyl Methyl Biazolon,** $C_6H_5.C_2N_2O_2.CH_3$ (see above), melts at 94° and boils at 280°.

The phenyl biazolons are quite stable towards acids, even when heated with the latter. Boiling alkalies decompose them into their components.

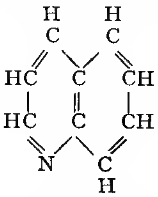
B. Derivatives of six-membered Nuclei, containing Nitrogen. Pyridine and Quinoline Group.

Pyridine, C_5H_5N, and Quinoline, C_9H_7N, are two basic bodies, which command particular interest, because they have been recognized as the parent substances of many alkaloids. In their entire deportment they closely resemble the benzene compounds. They are quite stable towards oxidizing agents (nitric acid, chromic acid, potassium permanganate). By replacing the hydrogen in them with alkyls (especially methyls) they yield a series of homologous compounds—the *Pyridine* and *Quinoline bases, e. g.*, $C_5H_4(CH_3)N$, and $C_5H_3(CH_3)_2N$, from which the acids (mono-, di- and tri-carboxylic acids) result on oxidizing the methyl groups. By elimination of the carboxyls from the acids, the stable parent nuclei, pyridine and quinoline, are regenerated. This deportment, characteristic of benzene compounds, is explained by the constitution of pyridine and quinoline. Both contain a closed chain consisting of five carbon-atoms and one nitrogen-atom. This ring is remarkably stable, and is very similar to the benzene ring.

Pyridine, C_5H_5N, may be regarded as a benzene in which one CH-group is replaced by a nitrogen-atom, whereas quinoline, C_9H_7N, is derived in a similar manner from naphthalene, $C_{10}H_8$, by a change in one of the benzene rings :—

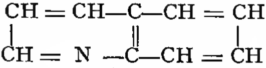


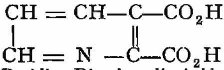
Pyridine.

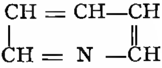


Quinoline.

These constitutional formulas have been proved by numerous syntheses of pyridine and quinoline, as well as of their derivatives (Körner, 1869). The formation of pyridine from quinoline is rather remarkable. The latter is oxidized, the benzene nucleus is destroyed (as with naphthalene, p. 907) the α- β-pyridine-dicarboxylic acid, $C_5H_3N(CO_2H)_2$, formed, and when it splits off $2CO_2$ pyridine is produced:—

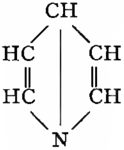

Quinoline.


Pyridine Dicarboxylic Acid.

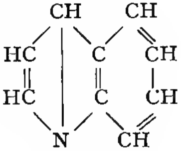

Pyridine.

Since the nitrogen-atom in the pyridine and quinoline bases is joined with three affinities to carbon, these compounds are tertiary amines, which combine with alkyl iodides, yielding ammonium iodides. Further, it follows, from the accepted structural formulas, that the pyridine and quinoline derivatives are capable, like benzene, of yielding hydrogen addition products; thus from pyridine, we obtain a hexa-hydride, $C_5H_5(H_6)N$, identical with the alkaloid piperidine, $C_5H_{11}N = C_5H_{10}:NH$.

Many of the transpositions of the pyridine nucleus, and the methods employed in its formation find their simplest explanation in the fact that the nitrogen atom present in the nucleus is in direct union with the carbon atom opposite to it (occupying the para position), as indicated in the formulas:—


Pyridine.

and


Quinoline.

(See *Berichte*, 17, 2871; 20, 801; 21, 1967). It is undetermined whether these prismatic or diagonal formulas are isomeric or tautomeric with the preceding ring-shaped formulas (as in analogous cases). In schemes showing the manner of union of the atoms in pyridine and quinoline—schemes analogous to the benzene hexagon—this difference disappears.

1. PYRIDINE GROUP—$C_nH_{2n-5}N$. [*]

PYRIDINE, C_5H_5N.

Picolines—$C_6H_7N = C_5H_4(CH_3)N$—Methyl pyridines.
Lutidines—$C_7H_9N = C_5H_3(CH_3)_2N$—Dimethyl pyridines.
Collidines—$C_8H_{11}N = C_5H_2(CH_3)_3N$—Trimethyl pyridines.

The following bases, isolated from coal-tar, have not been well studied and are included here: *Parvoline*, $C_9H_{13}N$ (B. P., 188°), *Corindine*, $C_{10}H_{15}N$ (at 211°), and *Rubidine*, $C_{11}H_{17}N$ (at 230°).

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[*] Buchka, Die Chemie des Pyridins und seiner Derivate, 1890.

The pyridine bases arise in the dry distillation of nitrogenous carbon compounds and occur simultaneously with the quinoline bases in coal-tar (along with the isomeric anilines) and especially in bone-oil.

To obtain the pyridine bases from Dippel's oil (p. 539), concentrate the dilute sulphuric acid solution (when any pyrrol which has dissolved will be volatilized or resinified), separate the pyridine bases by means of concentrated sodium hydroxide, dehydrate them with caustic soda and subject the product to fractional distillation (*Berichte*, 12, 1989). At present the pyridine bases are mainly obtained from coal-tar (*Annalen*, 247, 1). They occur in the "purifying acid," from which they can be easily isolated (*Berichte*, 20, 127; 21, 1006).

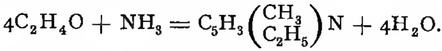
Again, the pyridines, as well as quinoline bases, are obtained by the distillation of the alkaloids (cinchonine) with caustic alkali, or by oxidizing the quinoline bases and alkaloids to pyridine carboxylic acids, *e. g.*, $C_5H_3N(CO_2H)_2$, which split off carbon dioxide (see above) and yield pyridines.

Synthetic methods for the production of the pyridines:—

(1) *β-Methyl Pyridine*, $C_5H_4(CH_3)N$, is prepared from acroleïn-ammonia, $C_6H_9.NO$, by elimination of water (p. 199), or by heating trichlor- or tribromallyl with alcoholic ammonia to 250°, and from glycerol and acetamide by heating with P_2O_5 (*Berichte*, 18, 3094):—

$$2C_3H_4O + NH_3 = C_5H_4(CH_3)N + 2H_2O.$$

(2) **(1, 4)-Methyl Ethyl Pyridine**, $C_5H_3(CH_3)(C_2H_5)N$, aldehyde collidine, aldehydine (p. 943), results when ethidene chloride or bromide is heated with alcoholic ammonia (*Berichte*, 18, 920), from aldehyde by the rearrangement of the oxytetraldine formed at first, but most readily from aldehyde ammonia upon heating it with paraldehyde (*Berichte*, 20, 444):—



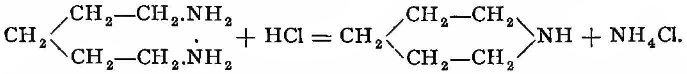
$$4C_2H_4O + NH_3 = C_5H_3\left(\begin{matrix}CH_3\\C_2H_5\end{matrix}\right)N + 4H_2O.$$

A methyl propylpyridine is analogously obtained from propionic aldehyde and acetamide (*Berichte*, 21, 279).

(3) The fact that chlor- and brom-pyridine can be produced by heating potassium pyrrol with $CHCl_3$ and $CHBr_3$ is of interest. Pyrrol and sodium ethylate may be used as a substitute for potassium pyrrol (*Berichte*, 18, 723). Pyridine results if CH_2I_2 be used (*Berichte*, 18, 3316); and with benzal chloride the product is β-phenylpyridine (*Berichte*, 20, 191). Pyridine and alkylpyridines (*Berichte*, 19, 2196) are similarly formed from α- and β-alkylpyrrols, $C_4H_3R.NH$ (p. 540) upon digesting them with concentrated hydrochloric acid. In all these reactions the entering C-atom assumes the β-position relatively to the pyrrol nitrogen (*Berichte*, 20, 194). The reaction occurs more readily by using pyrrolcarboxylic acid (*Berichte*, 21, 2856). Alkyl indols sustain similar transpositions; quinoline derivatives result.

(4) A very ready synthesis of the pyridine nucleus occurs upon heating penta-

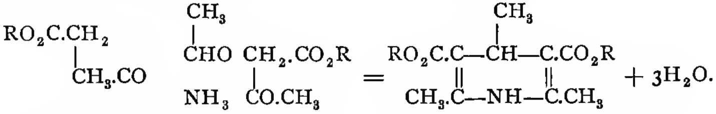
methylene diamine hydrochloride (p. 313); *piperidine* (hexhydropyridine) is produced (Ladenburg, *Berichte*, 18, 3100):—



Pyridine is formed when the piperidine is heated with concentrated sulphuric acid. Six hydrogen atoms are eliminated (p. 951). Trimethylenediamine yields trimethylenimine and β-methylpyridine (*Berichte*, 23, 2727).

(5) A method frequently pursued in synthesizing pyridine derivatives consists in the condensation of acetoacetic ester with an aldehyde-ammonia, or with an aldehyde and ammonia. This leads to the formation of dicarboxylic esters of alkyl dihydropyridines. Reaction of Hantzsch (*Annalen*, **215**, 1; *Berichte*, **18**, 2579).

(1, 3, 5)-**Trimethyldihydropyridine-dicarboxylic Ester** (dihydrocollidine dicarboxylic ester), $C_5H_2N(CH_3)_3(CO_2R)_2$, forms upon digesting acetoacetic ester (2 molecules) with aldehyde ammonia (1 molecule), or with acetaldehyde and ammonia:—



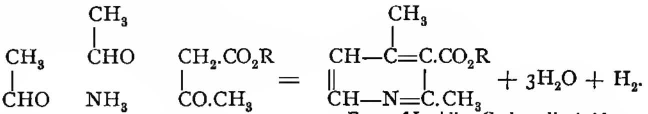
The entering aldehyde radical takes the para-position relatively to nitrogen (*Berichte*, 17, 1521). The three methyls occupy the positions (1, 3, 5), the two carboxyls are in (2, 4) (*Berichte*, 18, 1745). The two added hydrogen atoms are in union with the nitrogen and the γ-C-atoms (*Berichte*, 18, 2579 and 620). Nitrous acid oxidizes the dihydro compound to the ester of normal **Trimethyl-pyridine-carboxylic Acid**, $C_5N(CH_3)_3(CO_2R)_2$; this yields a series of pyridine derivatives.

The reaction proceeds in a perfectly analogous manner with propyl aldehyde, isobutyl aldehyde, *n*-butyl aldehyde and valeric aldehyde, with the formation of dimethyl alkyl derivatives, $C_5H_2N(CH_3)_2R(CO_2R)_2$ (*Berichte*, 21, Ref. 638). The aromatic aldehydes behave in the same way; benzaldehyde affords dimethyl-phenyl-dihydropyridine dicarboxylic ester (*Berichte*, 17, 1515). Cinnamic aldehyde (*Berichte*, 19, Ref. 18) and *m*-nitrobenzaldehyde react likewise. Primary amines act the same as ammonia; it is very probable that *n*-alkyl derivatives are produced in such cases. The ammonia can also be attached to acetoacetic ester. Paramidoacetoacetic ester (2 molecules), paraldehyde (1 molecule) and a little sulphuric acid form (1, 3, 5)-trimethyl-dihydropyridine-dicarboxylic ester:—$2C_6H_{11}NO_2 + C_2H_4O = C_{14}H_{21}NO_4 + NH_3 + H_2O$. On heating the para-amide ester alone, or its hydrochloride, we get oxy-dimethyl pyridine-monocarboxylic ester, $C_5H_2ON(CH_3)_2.CO_2R$, which, by the loss of the carboxyl group, forms pseudolutidostyril (p. 945) (*Berichte*, 21, 445).

Aceto-acetic ester reacts in the same manner with hexamethylenetetramine as with aldehydes and ammonia, the products being hydrolutidine dicarboxylic esters (*Berichte*, 21, 2740).

6. In Hantzsch's reaction one molecule of acetoacetic ester can be replaced by one molecule of aldehyde, the products then being dialkylmonocarboxylic esters. Thus, we obtain (1, 3)-**Dimethyl Pyridine-2-Carboxylic Ester** (*Berichte*, 18,

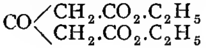
2020) on mixing acetoacetic ester (1 molecule) with aldehyde ammonia and acetaldehyde (1 molecule each):—



Ester of Lutidine Carboxylic Acid.

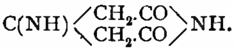
7. The pyrone derivatives (p. 958) may be rearranged to pyridine and oxypyridine compounds by heating them together with ammonia. This is an interesting reaction.

8. The rearrangement of acetone dicarboxylic ester by means of ammonia into oxyamido-glutaminic ester and glutazine, a derivative of trioxypyridine, is based upon analogous reactions (*Berichte*, 19, 2708; 20, 2655):—

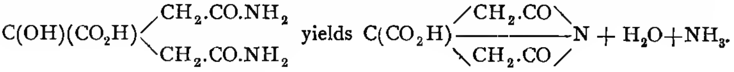


$$CO\left\langle\begin{matrix}CH_2.CO_2.C_2H_5\\CH_2.CO_2.C_2H_5\end{matrix}\right.$$

$$C(OH)(NH_2)\left\langle\begin{matrix}CH_2.CO.NH_2\\CH_2.CO_2.C_2H_5\end{matrix}\right.$$



Dioxypyridine carboxylic acid (citrazinic acid) (p. 947) is produced in a similar manner from citramide upon digesting it with sulphuric acid:—



The pyridine bases are colorless liquids with a peculiar odor. Pyridine, C_5H_5N, is miscible with water. The solubility of the higher members grows rapidly less. They form crystalline salts with one equivalent of the acids. They form double salts with mercuric and auric chlorides; these serve for the separation of the individual bases (*Annalen*, 247, 1). They are attacked with difficulty when boiled with nitric or chromic acid, and by this behavior are easily distinguished from the isomeric anilines. In the homologous pyridines, however, the alkyls are oxidized to carboxyls by a potassium permanganate solution.

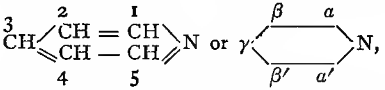
The pyridines combine, as tertiary bases with the alkyl iodides, yielding ammonium iodides (*Berichte*, 18, 591). The ammonium hydroxides, obtained from the latter by means of silver oxide, sustain a complicated decomposition when exposed to heat. Consult *Berichte*, 17, 1027, 19, 31, upon the deportment of the ammonium hydroxides of the pyridine-carboxylic acids.

If the ammonium iodides be heated with caustic soda, an extremely pungent odor is developed—*Reaction for the pyridine bases* (*Berichte*, 17, 1908). Some of the pyridines yield hydrides with nascent hydrogen (p. 937); their ammonium hydroxides are decomposed by further reactions into trimethylamine and a hydrocarbon (see piperidine and conine).

Pyridine heated with hydriodic acid to 300°, yields normal pentane, C_5H_{12}, and collidine, under the same treatment, yields normal octane (*Berichte*, 16, 591). Metallic sodium causes the pyridines to undergo a peculiar polymerization, and they then yield *dipyridine bases.*

Isomerides.

The derivatives produced by the replacement of the hydrogen atoms in pyridine can easily be deduced in their possible isomerisms from the given structural formulas (p. 937), and are perfectly analogous to the isomerisms of the benzene derivatives. Representing the five hydrogen atoms, or the affinities of the pyridine nucleus, with numbers or letters, corresponding to the diagram—

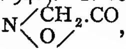


then the positions, 1 and 5, also 2 and 4 (as in benzene), are similar (p. 560). The first may be designated the ortho-, the latter, the meta-positions—while the position 3, occurring only once, corresponds to the *para* of benzene. From this we conclude, that the mono-derivatives of pyridine, $C_5H_4(X)N$, can exist in three series, while six isomerides are possible with the di-derivatives $C_5H_3(X_2)N$. This is verified by the existence of three methyl, three propyl- and phenyl-pyridines, $C_5H_4(R)N$, of three pyridine-mono-carboxylic acids, $C_5H_4(CO_2H)N$, of six dicarboxylic acids, etc. For practical reasons the isomerides are called α-, β-, and γ-derivatives, corresponding with the second diagram. α-Pyridine carboxylic acid (picolinic acid) corresponds to the position 1; the β-acid (nicotinic acid) to the position 2, and the γ-acid (isonicotinic acid) to position 3. This determination of place for the pyridine derivatives is evident from the manner in which the three phenyl pyridines, $C_5H_4(C_6H_5)N$, are produced, the α- and β- being derived from the two naphthoquinolines. See Skraup, Monatshefte für Chemie, IV, 437, 595 and *Berichte*, 17, 1518; 18, 1745.

The behavior of the pyridine dicarboxylic acids, $C_5H_3N(CO_2H)_2$, leads to a simpler deduction of the position of their atoms (Ladenburg, *Berichte*, 18, 2967). The ortho-position of α-oxypyridine is evident from the fact that it can be formed by oxidizing carbostyril (*Berichte*, 19, 2432). Quinolinic acid (pyridine carboxylic acid), formed by the oxidation of quinoline, has the position (1, 2), and cinchomeronic acid, from isoquinoline, has the position (2, 3). Quinolinic acid loses one molecule of carbon dioxide when heated and forms nicotinic acid, while cinchomeronic acid yields nicotinic acid and isonicotinic acid; therefore nicotinic acid is $\beta = 2$ and isonicotinic acid $\gamma = 3$.

Pyridine, C_5H_5N, can be prepared from bone-oil, and is obtained from all the pyridine-carboxylic acids on distillation with lime. It is a pungent-smelling liquid, miscible with water, of sp. gr. 1.0033 at 0°, and boiling at 114.8°. Its hydrochloride, $C_5H_5N.HCl$, is deliquescent, and with platinum chloride it forms a double salt, $(C_5H_5N.HCl)_2.PtCl_4$, that is rather insoluble. Sodium amalgam, or better, sodium and alcohol, convert it into the hexahydride—

piperidine, $C_5H_{10}N$ (p. 950), from which, vice versa, pyridine is obtained by oxidation.

Pyridine forms ammonium iodides with alkyl iodides (p. 940). It combines with chloracetic acid and yields **Pyridine-betaïne,**  $C_5H_5N\left\langle\begin{array}{l}CH_2.CO\\O\end{array}\right\rangle$, corresponding fully to ordinary betaïne. The homologous pyridines yield analogous betaïnes (*Berichte*, 23, 2609).

Sodium converts pyridine into polymeric **Dipyridine,** $C_{10}H_{10}N_2$, an oil boiling at 286–290°; potassium permanganate oxidizes it to isonicotinic acid. At the same time rather large quantities of *p*-**Dipyridyl,** $C_{10}H_8N_2 = NC_5H_4.C_5H_4N$ ($\gamma\gamma$), are produced; this distils at 304°, sublimes in long needles, and melts at 114°. It crystallizes from water containing two molecules of water and melts at 73°. It is a di-acid base. Potassium permanganate oxidizes it to isonicotinic acid. *Isonicotine,* $C_{10}H_{14}N_2$, is obtained from it by reduction with tin and hydrochloric acid. Isomeric *m*-**Dipyridyl,** $C_{10}H_8N_2$ ($\beta\beta$), results from meta-dipyridyl-dicarboxylic acid (from phenanthroline, p. 950), boils at 287°, and yields deliquescent needles, melting at 68°. Potassium permanganate oxidizes it to nicotinic acid. Reduction with tin and hydrochloric acid produces *nicotidine.* A third **Dipyridyl** ($\alpha\alpha$) has been prepared by the distillation of copper picolinate. It melts at 70° (*Berichte*, 21, 1077).

Substitution Products.—Pyridine and its homologues are substituted with difficulty by the halogens (*Berichte*, 21, 1773). Nitro products have not been prepared. Bromine acts more readily upon pyridine sulphonic and carboxylic acids, especially upon the application of heat. The side-chains are then replaced (*Berichte*, 20, 1343). *β-Chlor-* and *Brom-pyridine* have been synthetically prepared from pyrrol by means of chloroform, etc. (p. 938).

If pyridine (or piperidine) be heated with concentrated sulphuric acid to 330°, or with fuming sulphuric acid we get β-**Pyridine-sulphonic** and **disulphonic acids,** $C_5H_4N(SO_3H)$, and $C_5H_3N(SO_3H)_2$, which form needles that dissolve without difficulty. β-**Cyan-pyridine,** $C_5H_4N.CN$, produced on distilling the sodium salt with potassium cyanide, crystallizes in white needles, melts at 48–49°, and by saponification yields nicotinic acid.

Homologous Pyridines.

The methylated pyridines occur in bone-oil and coal tar. They are synthetically prepared by heating the pyridine-ammonium-iodides to 300° (Ladenburg, *Berichte*, 17, 772):—

$$C_5H_5N.C_2H_5I = C_5H_4(C_2H_5)N.HI.$$

This is analogous to the formation of the homologous anilines from the alkyl anilines (p. 601). They also result from the alkyl piperidines by the splitting-off of hydrogen when heated with concentrated sulphuric acid (p. 951). Conversely, nascent hydrogen (best from metallic sodium and alcohol) converts them into alkyl piperidines.

Higher alkyl pyridines, with unsaturated side-chains, may be synthesized by condensing α-methyl pyridines and aldehydes. This can be effected by means of zinc chloride. Thus, paraldehyde yields *a*-allyl pyridine, $C_5NH_4.CH:CH.CH_3$, benzaldehyde forms *Stilbazole*, $C_5NH_4.CH:CH.C_6H_5$ (analogous to stilbene), while ethyl-*a*-methyl pyridine yields ethyl-*a*-stilbazole (*Berichte*, 21, 818, 3099). *a*-Methyl pyridine and methylal yield, rather singularly, dipicolylmethane, $CH_2(CH_2.C_5H_4N)_2$.

An aldol condensation sometimes occurs between *a*-methyl pyridine and the aldehydes. Bases with hydroxylated side-chains are then produced; these are called *Alkines and Tropines* (Ladenburg, *Berichte*, 22, 2583; 23, 2709):—

$$C_5H_4N.CH_3 + CH_2O = \underset{a\text{-Picolyl alkine.}}{C_5H_4N.CH_2.CH_2.OH.}$$

a-Picolyl methyl alkine, $C_5H_4N.CH_2.CH(OH).CH_3$, is similarly obtained with ethyl aldehyde, etc.

1. Methyl Pyridines, $C_5H_4(CH_3)N$, Picolines.

a- and *β*-**Methyl Pyridine** occur in bone oil, and may be separated by means of their $PtCl_4$ salts (*Annalen*, 247, 5). The *β*-body has been obtained artificially by different reactions. *a*-Picoline results when pyridine is methylated. It boils at 130°; its sp. gr. is 0.965 at 0°, and it is oxidized by potassium permanganate to picolinic acid; the *β*-body boils at 143°, and yields nicotinic acid. The picoline formed when strychnine is distilled is identical with *β*-picoline (*Berichte*, 23, 3151). *γ*-**Methyl Pyridine**, from coal tar, is produced when methyl pyridine iodide is heated to 290°. It boils at 144°. Its sp. gr. is 0.974 at 0°. It yields isonicotinic acid when it is oxidized (*Annalen*, 247, 11).

Sodium and alcohol convert the three methyl pyridines into methyl piperidines.

2. Dimethylpyridines, $C_5H_3(CH_3)_2N$, Lutidines.

There are six isomerides. Several occur in that fraction of bone-oil boiling at 150–170°. *aa*-Lutidine occurs in the greatest abundance; associated with it are *aγ*- and *aβ*-lutidines (*Berichte*, 21, 1006). *aa*-Lutidine boils at 142°; its specific gravity is 0.942 at 0°. It yields *aa*-pyridine carboxylic acid when oxidized (*Annalen*, 247, 28). *aγ-Lutidine*, from coal tar, boils at 157°; its sp. gr. is 0.9493 at 0°. It yields *aγ*-pyridine dicarboxylic acid when oxidized. *ββ*-Lutidine, from the corresponding dimethyl pyridine carboxylic acid, boils at 170°, and when oxidized becomes dinicotinic acid (*Berichte*, 23, 1113).

3. Ethyl Pyridines, $C_5H_4(C_2H_5)N$.

a-**Ethyl pyridine** is prepared, together with the *γ*-, on heating pyridine-ethyl iodide (to 290°). It boils at 148°; its sp. gr. is 0.949 at 0°, and yields picolinic acid when oxidized (*Annalen*, 247, 13). *β*-**Ethyl pyridine** has been obtained from cinchonine and brucine on heating with caustic potash. It boils at 166°, and yields nicotinic acid when oxidized. *γ*-**Ethyl pyridine**, produced together with the *a*- and *β*-, boils at 165°, and yields isonicotinic acid when oxidized. Its sp. gr. is 0.952 at 0°. Sodium and alcohol convert all three isomerides into ethyl piperidines.

4. Trimethyl Pyridines, $C_5H_2(CH_3)_3N$, Collidines.

Sym. (1, 3, 5)- collidine was first obtained by distilling sym. collidine dicarboxylic acid with lime. It is present in coal tar. It boils at 172°, and turns brown on exposure to the air. When oxidized it yields pyridine tricarboxylic acid (*Berichte*, 20, Ref. 106; *Annalen*, 21, 1011).

(1,4)- **Methyl-Ethyl Pyridine**, $C_5H_3(CH_3)(C_2H_5)N$, has been prepared from various aldehyde compounds, hence called *aldehydine* or *aldehydcollidine*. It boils at 178°, and when oxidized forms (1, 4)- pyridine-dicarboxylic acid

(*Annalen*, 247, 41). See *Annalen*, 247, 46, for two additional methyl ethyl pyridines.

Propyl Pyridines, $C_5H_4(C_3H_7)N$.

α-**Propyl Pyridine, Conyrine,** is produced on heating conine hydrochloride with zinc dust, and is obtained on heating inactive α-propyl piperidine (*Annalen*, 247, 20). It is a bright blue, flourescent oil, boiling at 167°. If oxidized, it yields picolinic acid. Heated with hydriodic acid it again forms conine.

β-**Propyl Pyridine** appears to be a base, formed by distilling nicotine, $C_{14}H_{11}N_2$, through an ignited tube. It boils at 170°, and is oxidized to nicotinic acid.

α-**Isopropyl Pyridine,** $C_5H_4(C_3H_7)N$, is produced together with the γ-compound when pyridine propyl iodide or isopropyl iodide is heated to 290° (*Annalen*, 247, 22). It boils at 158°. When oxidized it forms picolinic acid. Sodium and alcohol change it to isopropyl piperidine (p. 952). γ-Isopropyl pyridine boils at 177°, and yields isonicotinic acid when oxidized (p. 946). See *Berichte*, 23, 685, for the dimethyl ethyl pyridine, obtained from propionic aldehyde.

α-**Vinyl Pyridine,** $C_5H_4(C_2H_3)N$, results when pyridine vapors are conducted together with ethylene through a tube heated to redness, as well as from α-picolyl alkine by the loss of water, and from pyridine acrylic acid. It is a liquid with a sweet odor, and boils at 160°. It yields picolinic acid when oxidized (*Berichte*, 20, 1644).

α-**Allyl Pyridine,** $C_5H_4(C_3H_5)N$, is produced when α-picoline and paraldehyde are heated to 200° (*Annalen*, 247, 26). Its odor is like that of conyrine. It boils at 190°. Sodium and alcohol convert it into α-propyl piperidine (inactive conine, p. 952).

Phenyl Pyridines, $C_5H_4(C_6H_5)N$.

α- and β-**Phenyl pyridine** have been obtained from α- and β-naphtho-quinoline (see these). By the oxidation of the latter we get α- and β phenyl-pyridine-dicarboxylic acids, $C_5H_3N\left\{\begin{matrix} C_6H_4.CO_2H \\ CO_2H \end{matrix}\right.$, and when $2CO_2$ split off from these the phenyl pyridines are produced (p. 950).

α-*Phenyl pyridine* boils at 267°, and when oxidized with chromic acid yields picolinic acid; β-phenyl pyridine boils at 270°, and yields nicotinic acid.

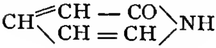
γ-**Phenyl pyridine,** formed from aceto-acetic ester, etc. (p. 939), boils at 275°, and yields isonicotinic acid by oxidation. It consists of colorless needles melting at 77°. Metallic sodium and alcohol reduce it to γ-phenyl piperidine (p. 952).

Pyridyl Alkines (p. 943).

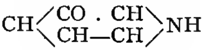
α-**Picolyl Alkine,** $C_5NH_4.CH_2.CH_2.OH$, from α-picoline and formic aldehyde, is a thick syrup, boiling at 179° under 22 mm. pressure. α-*Picolyl methyl-alkine*, $C_5H_4N.CH_2.CH(OH).CH_3$, derived from acetaldehyde, boils at 179° under 18 mm. pressure. For additional pyridyl alkines consult *Berichte*, 23, 2709, 2725.

Oxy-derivatives of the Pyridines.

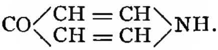
These resemble the phenols in deportment, especially the amidophenols. They are formed by analogous reactions, with special ease from the oxypyridine carboxylic acids by the elimination of the carboxyl groups. They form salts with bases and acids. Ferric chloride imparts a red color to nearly all their solutions. On the other hand, different oxypiperidines and oxypiperidinic acids manifest the deportment of imides or lactams. They must be viewed as *keto* or *aci*-compounds of the dihydro-pyridines, and are called therefore *pyridones* (lutidones), corresponding to the formulas:—


$$CH\left\langle\begin{array}{l}=CH-CO\\ CH=CH\end{array}\right\rangle NH$$

α-Pyridone.


$$CH\left\langle\begin{array}{l}CO\,.\,CH\\ CH-CH\end{array}\right\rangle NH$$

β-Pyridone (?)


$$CO\left\langle\begin{array}{l}CH=CH\\ CH=CH\end{array}\right\rangle NH.$$

γ-Pyridone.

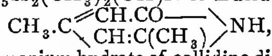
It is undetermined whether these formulas are isomeric or tautomeric with the hydroxyl formulas. However, isomeric alkyl compounds of both types are known (*Berichte*, 22, 73).

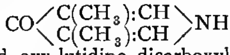
1. *Oxypyridines*, $C_5H_4(OH)N$ or *Pyridones*. Three Isomerides. *α-Oxypyridine, α-Pyridone* (1 = 5), is obtained from oxyquinolinic acid (p. 948) and from oxy-nicotinic acid (from coumalic acid, p. 947), by the elimination of carbon dioxide (*Berichte*, 18, 317; 19, 2433). It dissolves readily in water and alcohol, crystallizes in needles, melting at 106°. Ferric chloride colors it red. Bromine water converts it into a dibromoxypyridine, $C_5H_2Br_2(OH)N$, melting at 206°.

β-**Oxypyridine** is formed when β-pyridine sulphonic acid is fused with caustic potash. It is very soluble in water and alcohol, crystallizes in needles, melts at 124°, and can be distilled without decomposition. Its *ethyl ether*, $C_5H_4(O.C_2H_5)N$, is produced by the action of alcoholic potash upon β-brompyridine. Hydriodic acid again decomposes it, at 110°, into β-oxypyridine (*Berichte*, 17, 1896; 18, Ref. 634).

γ-**Oxypyridine**, γ-**Pyridone**, is produced by heating oxypicolinic acid (from comanic acid, p. 958) and ammon-chelidonic acid. It is very soluble in water, soluble with difficulty in ether, crystallizes in plates with $1H_2O$, and when anhydrous melts at 148°. Ferric chloride colors it yellow. Methyl iodide converts it into the hydroiodide of *n*-methyl pyridone, a crystalline mass, melting at 89°. It can also be obtained from methyl ammon-chelidonic acid, hence its methyl group is attached to nitrogen. Hydriodic acid does not even decompose it at 165°. *γ-Methoxy-pyridine*, $C_5H_4(O.CH_3)N$, is isomeric with it. This compound may be prepared by heating chlorpyridine with sodium ethylate. It boils at 190°, reacts alkaline, and is broken down when heated to 100° with hydriodic acid (*Berichte*, 18, 930, Ref. 382).

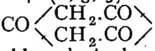
2. **Oxylutidines**, $C_5H_2(CH_3)_2(OH)N$ or **Lutidones**, $C_5H_2O(CH_3)_2NH$.

Pseudo-lutido-styril,  $CH_3.C\left\langle\begin{array}{l}=CH.CO\text{——}\\ CH{:}C(CH_3)\end{array}\right\rangle NH$, (3, 5)-*Dimethyl-α-pyridone*, is obtained from the ammonium hydrate of collidine dicarboxylic ester, $C_5(CH_3)_3N(CO_2.C_2H_5)_2$ (p. 949), by a complex transposition (*Berichte*, 17, 2903); and also from the amido-aceto-acetic ester condensation product (p. 940) (*Berichte*, 22, 447). It crystallizes in minute needles, that melt at 180° and boil about 305°. It forms (1, 3)-lutidine when distilled with zinc dust.

(2, 6)-*Dimethyl-γ-pyridone*,  $CO\left\langle\begin{array}{l}C(CH_3){:}CH\\ C(CH_3){:}CH\end{array}\right\rangle NH$, *γ-Lutidone*, results from lutidone dicarboxylic acid and oxy-lutidine dicarboxylic acid by the elimination of the carboxyl groups. It crystallizes with 1½ molecules of water; when anhydrous it melts at 225° and boils at 350° (*Berichte*, 20, 156). It forms (2, 4)-lutidine when distilled with zinc dust.

3. **Dioxypyridines**, $C_5H_3(OH)_2N$.

Three isomeric bodies have been obtained from pyridine disulphonic acid, dibrom-pyridine and dioxypicolinic acid (*Berichte*, 18, Ref. 633).



4. (1, 3, 5)-**Trioxypyridine**, $C_5H_2(OH)_3N$, or **Triketohexahydropyridine**, $CO\left\langle\begin{matrix}CH_2.CO\\CH_2.CO\end{matrix}\right\rangle NH$, Triketopiperidine, bears the same relation to pyridine that phloroglucin bears to benzene (p. 695). It can be obtained by boiling glutazine with hydrochloric acid. It is a microcrystalline yellow product, that swells up at 220–230° and then decomposes. Heated with ammonia it forms **Glutazine**, $C_5H_6N_2$; which can also be prepared by heating acetone dicarboxylic ester with ammonia (p. 940) (*Berichte*, 19, 2708; 20, 2655).

Pyromecazonic Acid, $C_5H_2(OH)_3N$, is an isomeric trioxpyridine, obtained from pyromeconic acid. Ferric chloride colors it a dark indigo blue.

Pyridine Carboxyl Compounds.

The pyridine carboxylic acids are obtained from the homologous pyridines by oxidizing them with potassium permanganate, and are also formed by oxidizing the quinolines and alkaloids (with nitric acid, chromic acid or potassium permanganate). The lower acids can be prepared from the polycarboxylic acids, *e.g.*, $C_5(CH_3)_3N(CO_2H)_2$ and $C_5N(CO_2H)_5$, by the partial elimination of single carboxyls, and by completely removing the latter (by heating with lime) all the acids yield pyridine or its homologues. As these acids represent combinations of carboxyl with the basic pyridine radical, they therein manifest a deportment analogous to that of the amido-acids, and are also capable of forming salts with acids. The basic character of these acids diminishes with the increase in number of carboxyls, and disappears entirely in the penta-carboxylic acid. Those pyridine- (and quinoline) carboxylic acids, containing a carboxyl in the α-position, are colored red by ferrous sulphate.

1. *Pyridine-mono-carboxylic Acids*, $C_6H_5NO_2 = C_5H_4N(CO_2H)$.

α-**Pyridine-carboxylic Acid** (1 or ortho), **Picolinic Acid**, was first obtained by the oxidation of α-picoline. It is very readily soluble in alcohol and water, crystallizes in white needles, which melt at 135–136°, and sublime. Ferrous sulphate imparts a faint yellow color to their solutions. By the action of sodium amalgam, ammonia is split off, and the acid, $C_6H_8O_3$, formed; this melts at 85°.

β-**Pyridine Carboxylic Acid** (2 or meta), **Nicotinic Acid**, was first obtained by oxidizing nicotine. It is also prepared from β-methyl and ethyl pyridine, from β-cyanpyridine and from the three pyridine dicarboxylic acids (quinolinic, cinchomeronic and isocinchomeronic acids) by the elimination of a CO_2-group. The easiest course to pursue in preparing the acid consists in heating quinolinic acid with hydrochloric acid to 180°. It crystallizes from hot water in needles or warty masses, and melts at 228–229°.

γ-**Pyridine-carboxylic Acid** (3 or para), **Isonicotinic Acid**, is obtained by oxidizing γ-methyl- and ethyl-pyridine, and from the dicarboxylic acids, cinchomeronic and lutidinic acids, by the splitting-off of CO_2. It is almost insoluble in hot alcohol, forms fine needles when crystallized from hot water, and sublimes in small plates without previous melting. When heated in a closed tube it melts at 304°.

Pyridine Fatty Acids.

The known acids of this group are α-pyridyl acrylic acid and α-pyridyl lactic acid, which appear to be closely related to anhydroecgonine and ecgonine—derivatives of cocaïne (*Berichte*, 23, 224).

α-**Pyridyl Acrylic Acid**, $C_5H_4N.CH:CH.CO_2H$, is formed together with α-pyridyl lactic acid from the condensation product of α-picoline and chloral by the action of caustic potash. It crystallizes in minute needles, melting at 202°. *α-Pyridyl Lactic Acid*, $C_5H_4N.CH_2.CH(OH).CO_2H$, consists of fine needles, melting at 146°.

Oxypyridine Monocarboxylic Acids.

γ-**Oxypicolinic Acid**, $C_5H_3(OH)N(CO_2H)$ ($\gamma\alpha$), has been obtained, in a synthetic manner, from comanic acid, (p. 958), on digesting with ammonia. It crystallizes in shining leaflets, containing one molecule of water. It melts at 250°, and decomposes into CO_2 and γ-pyridone (p. 945).

α'-**Oxynicotinic Acid**, $C_5H_3(OH)N(CO_2H)(\alpha'\beta)$ or *α-Pyridone-β'*-carbóxylic acid, $C_5H_3O(NH)CO_2H$ (p. 945), is produced when ammonia acts upon coumalic acid ester (*Berichte*, 17, 2390); also when oxyquinolinic acid (p. 948) is heated to 200°. It dissolves with difficulty in water and alcohol, crystallizes in delicate needles, and melts at 303°, breaking down at the same time into CO_2 and α-pyridone. Sodium amalgam eliminates its nitrogen as ammonia. *Methyl-oxy nicotinic acid* is obtained from it by the action of methyl iodide and caustic potash. This acid can also be derived from coumalic acid by means of methylamine. Sodium amalgam will cause it to split off methylamine. Therefore, its methyl group is attached to nitrogen, and the acid is an *α-methylpyridon* carboxylic acid, $C_5H_3O(N.CH_3).CO_2H$ (*Berichte*, 18, 318).

Dioxypicolinic Acid, $C_5H_2(OH)_2N(CO_2H)$, *Comenamic Acid*, is derived from comenic acid (p. 959) by aid of ammonia. It crystallizes in plates, containing two molecules of water. Ferric chloride imparts a purple-red color to its solution. Oxalimide (p. 407) is obtained from it by the action of nitrous acid in glacial acetic acid (*Berichte*, 19, 3228).

Dioxyisonicotinic Acid, $C_5H_2(OH)_2N(CO_2H)$, *Citrazinic Acid*, is formed when citramide is heated with hydrochloric or sulphuric acid. It is a bright yellow insoluble powder, which decomposes without melting on being heated beyond 300°. Its alkaline solution acquires a deep blue color on exposure to the air. It yields γ-pyridine carboxylic acid by the reduction of its hydroxyl groups. See *Berichte*, 23, 831, as to its constitution.

Methyl Pyridine Monocarboxylic Acids.

$\alpha\gamma$-**Picoline Carboxylic Acid**, $C_5H_3(CH_3)N(CO_2H)$(CH_3 in γ), is obtained on heating uvitonic acid (p. 949) to 280°. It sublimes without previously fusing, and when oxidized becomes lutidinic acid (p. 948).

$\beta\gamma$-**Methyl-Pyridine-Carboxylic Acid** (CH_3 in γ) results on heating methyl quinolinic acid to 170°, or when it is boiled with glacial acetic acid. It melts at 209–210°, and is oxidized to cinchomeronic acid.

Lutidine Carboxylic Acid, $C_5H_2(CH_3)_2N(CO_2H)$($\alpha\beta\gamma$-CO_2H in β). Its *ethyl ester* results in the condensation of aceto-acetic ester with aldehyde and aldehyde-ammonia (p. 939). The free acid contains two molecules of water of crystallization, yields $\alpha\gamma$-lutidine by the elimination of carbon dioxide, and when oxidized forms $\alpha\beta\gamma$-pyridine tricarboxylic acid (p. 949).

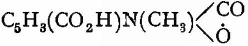
2. *Pyridine Dicarboxylic Acids*, $C_7H_5NO_4 = C_5H_3N(CO_2H)_2$.

The six possible isomerides (p. 941) are known (*Berichte*, 19, 293).

1. **Quinolinic Acid** ($\alpha\beta$ or 1, 2) is obtained from quinoline and from 1 and 4 methyl-quinoline by oxidation with potassium permanganate (*Berichte*, 19, 31).

It is sparingly soluble in water and alcohol, crystallizes in shining, short prisms, melts at 190°, and decomposes (by slowly heating to 160°) into CO_2 and nicotinic acid (*Berichte*, 19, 2767). Ferrous sulphate imparts a reddish-yellow color to its solution. Its *anhydride* is produced when it is heated with acetic anhydride. This melts at 134°. Its derivatives are similar to those formed by phthalic anhydride (*Berichte*, 20, 1209).

2. **Cinchomeronic Acid** ($\beta\gamma$ or 2, 3) is obtained from quinine, cinchonine and cinchonidine, by oxidation with nitric acid and by the oxidation of $\beta\gamma$-methyl-pyridine carboxylic acid with potassium permanganate. It also results from pyridine tricarboxylic acid and from apophyllenic acid. It crystallizes from water in prisms containing hydrochloric acid, and melts at 266°, with decomposition into CO_2, γ-pyridine carboxylic acid and a little nicotinic acid. When heated with acetic anhydride it yields its *anhydride*, $C_5H_3N(CO)_2O$, melting at 67°. Sodium amalgam decomposes it into NH_3 and cinchonic acid, $C_7H_6O_5$, which breaks up into CO_2, and dimethylfumaric anhydride (p. 430) on application of heat (*Berichte*, 18, 2968).

Cotarnine, $C_{12}H_{13}NO_3$, boiled with nitric acid, yields **Apophyllenic Acid**, $C_8H_7NO_4$ (*Berichte*, 19, Ref. 706). This is methylated cinchomeronic acid, in which the methyl group is attached to the nitrogen atom, and has the formula,  $C_5H_3(CO_2H)N(CH_3){<}\begin{array}{l}CO\\ \vert\\ O\end{array}$ (comp. betaïne, p. 316). It melts with decomposition at 242°, and when heated to 250° with hydrochloric acid decomposes into methyl chloride and cinchomeronic acid.

3. **Lutidinic Acid** ($a\gamma$ or 1, 3) is produced together with isocinchomeronic acid by oxidizing $a\gamma$-lutidine and picoline carboxylic acid with potassium permanganate (*Annalen*, 247, 37). It crystallizes with a molecule of water in microscopic needles, receives a blood-red color from ferrous sulphate, melts at 235°, and breaks up into CO_2 and γ-pyridine carboxylic acid.

4. **Isocinchomeronic Acid** ($a\beta' = 1, 4$) is obtained from pyridine tricarboxylic acid (*Berichte*, 19, 1311) and aldehyde collidine. It crystallizes from acidulated hot water, with one or one and a half molecules of water, in microscopic leaflets, which melt at 236°, and when heated to 220° together with glacial acetic acid decomposes into CO_2 and nicotinic acid. Ferrous sulphate imparts a reddish-yellow color to the solution.

5. **Dipicolinic Acid** ($aa' = 1, 5$) results when aa'-lutidine (p. 943) is oxidized with potassium permanganate (*Annalen*, 247, 33). It crystallizes in shining leaflets, melts at 225°, and at 227° decomposes into two molecules of carbon dioxide and pyridine (together with a slight amount of picolinic acid).

6. **Dinicotinic Acid** ($\beta\beta' = 2, 4$) may be prepared from symmetrical pyridine tetracarboxylic acid, from (1, 2, 4)-pyridine tricarboxylic acid on boiling with glacial acetic acid (*Berichte*, 19, 286), and from $\beta\beta$-lutidine (p. 943). It dissolves with difficulty in water, consists of minute crystals, melts at 314°, and breaks down into carbon dioxide and nicotinic acid (*Berichte*, 23, 1114).

Oxypyridine Dicarboxylic Acids, $C_5H_2(OH)N(CO_2H)_2$.

a-**Oxyquinolinic Acid** (1, 2, 5—OH in 5), obtained by fusing quinolinic acid with KOH (*Berichte*, 16, 2158), also from amidocarbostyril by oxidation with permanganate (*Berichte*, 19, 2432), consists of thick crystals, which char at 254°, but do not melt. When heated to 195° with water it decomposes into carbon dioxide and oxypyridine carboxylic acid (see above); the silver salt yields a-oxy-pyridine when heated. Ferric chloride colors it a deep red.

Ammon-chelidonic Acid (1, 5, 3—OH in 3), *chelidamic acid*, formed from chelidonic acid with ammonia, is a white, rather insoluble powder that breaks down into carbon dioxide and γ-pyridone when heated above 230°.

Methyl Ammon-chelidonic Acid, $C_5H_2O(N.CH_3)(CO_2H)_2$, obtained by the aid of methylamine, yields *n*-methyl pyridone by decomposition (p. 945).

Picoline Dicarboxylic Acids, $C_5H_2(CH_3)N(CO_2H)_2$.

1. **Methyl-quinolinic Acid** (1, 2, 3—CH_3 in 3) is produced upon oxidizing γ-methyl-quinoline with potassium permanganate, as an intermediate product to the tricarboxylic acid. It crystallizes from water in plates or prisms, is colored yellow by ferrous sulphate, melts about 186° with decomposition, and yields (even on boiling with glacial acetic acid) carbon dioxide and βγ-methylpyridine carboxylic acid (p. 947).

2. **Uvitonic Acid** is formed when ammonia acts upon pyroracemic acid, consists of microscopic leaflets, is colored violet-red by ferrous sulphate, melts at 244°, and above 280° decomposes into CO_2 and picoline-carboxylic acid.

(1, 3, 5)-Trimethyl-(2, 4)-pyridine Dicarboxylic Acid, $C_5(CH_3)_3N(CO_2H)_2$, Collidine dicarboxylic acid. The *diethyl ester* is prepared by the oxidation of dihydro-collidine dicarboxylic ester (from aceto-acetic ester with aldehyde ammonia, (p. 939) in alcholic solution with nitrous acid. The free acid, obtained by saponifying the ester, crystallizes in little needles, and decomposes when strongly heated without melting. Distilled with lime it yields a (1, 3, 5)-trimethyl pyridine (p. 943). By successively oxidizing its methyl groups with potassium permanganate we obtain: **lutidine tricarboxylic acid**, $C_5(CH_3)_2N(CO_2H)_3$, **picoline-tetracarboxylic acid**, $C_5(CH_3)N(CO_2H)_4$, and **pyridine pentacarboxylic acid**, $C_5N(CO_2H)_5$. The separation of but one carboxyl from collidine-dicarboxylic acid yields **collidine-monocarboxylic acid**, $C_5H(CH_3)_3N(CO_2H)$ (*Annalen*, 225, 133), which by successive oxidation forms **lutidine-dicarboxylic acid**, $(C_5H(CH_3)_2N(CO_2H)_2$, **picoline-tricarboxylic acid**, $C_5H(CH_3)N(CO_2H)_3$, and **pyridine-tetracarboxylic acid**, $C_5HN(CO_2H)_4$.

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(3) *Pyridine Tricarboxylic Acids*, $C_8H_5NO_6 = C_5H_2N(CO_2H)_3$.

1. αβγ-**Pyridine Tricarboxylic acid** (1, 2, 3) (tricarbopyridinic acid, carbocinchomeronic acid), is obtained by completely oxidizing quinine, cinchonine, quinidine and cinchonidine, with potassium permanganate, and by the same treatment of γ-methyl quinoline, methyl-quinolinic acid (see above) and cinchoninic acid (p. 972). It is very soluble in hot water, crystallizes in plates with 1½ molecules of H_2O, becomes anhydrous at 115–120°, chars and melts when rapidly heated at 249–250°, with decomposition. At 180° it gradually breaks up (more readily on boiling with glacial acetic acid) into carbon dioxide and cinchomeronic acid. Ferrous sulphate gives it a faint red color. It is very probably identical with **Berberonic Acid**, formed from the alkaloid berberine by oxidation.

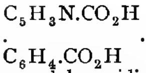
2. αββ′-**Pyridine Tricarboxylic Acid** (1, 2, 4) is obtained from β-ethyl quinoline and β-quinoline-carboxylic acid by oxidation with MnO_4K. It is colored reddish-yellow by ferrous sulphate, and softens with liberation of CO_2, about 145° (p. 948). It is very soluble in water and forms needles on crystallizing.

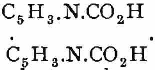
3. Symmetrical *ααγ- Pyridine Tricarboxylic Acid* (1, 3, 5) is obtained upon oxidizing symmetrical collidine (p. 943) and uvitonic acid (see above) with potassium permanganate. It crystallizes with two molecules of water. In an anhydrous state it melts at 227°, with decomposition into carbon dioxide and isonicotinic acid (*Annalen*, 228, 29). *ααβ-Pyridine Dicarboxylic Acid* (1, 2, 5) results when the corresponding lutidine carboxylic acid is oxidized with potassium permanganate. It crystallizes in leaflets containing two molecules of water. It melts at 100° in its water of crystallization, and at 130° breaks down into carbon dioxide and isocinchomeronic acid (*Berichte*, 19, 1309).

4. *Pyridine Tetra-Carboxylic Acids*, $C_9H_5NO_8 = C_5HN(CO_2H)_4$.

The *ααβγ-Acid* is produced in the oxidation of collidine carboxylic acid and flavenol (p. 971). It forms needles, containing two molecules of water. It loses water very slowly above 115°, and when anhydrous melts at 227°. Ferric chloride colors it cherry-red (*Berichte*, 17, 2927). Symmetrical *ααββ-acid* is derived from the corresponding lutidine dicarboxylic acid (from aceto-acetic ester and isobutylaldehyde etc.) by oxidation. It consists of minute needles, containing one molecule of water, and at 150° breaks down into carbon dioxide and dinicotinic acid. Ferrous sulphate imparts a blood-red coloration to its solution (*Berichte*, 19, 284).

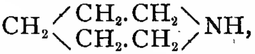
5. **Pyridine Pentacarboxylic Acid**, $C_5N(CO_2H)_5 = C_{10}H_5NO_{10}$, is formed by the oxidation of synthetic collidine dicarboxylic acid and from the acids obtained in its oxidation. It crystallizes in microscopic needles, containing two molecules of water. It dissolves very readily in water, blackens at 200°, and decomposes, without melting, at 220°. Ferrous chloride imparts to its solutions a dark red color.

Phenylpyridine Dicarboxylic Acids,  $\begin{array}{l} C_5H_3N.CO_2H \\ \vert \\ C_6H_4.CO_2H \end{array}$. There are two isomeric acids, α- and β-, which have been prepared by oxidizing α- and β-naphthoquinoline (p. 974) with potassium permanganate. They yield α- and γ-phenylpyridine by the loss of two molecules of carbon dioxide.

Dipyridyl-dicarbonic Acids,  $\begin{array}{l} C_5H_3.N.CO_2H \\ \vert \\ C_5H_3.N.CO_2H \end{array}$. Two isomeric acids, α- and β-, have been formed by oxidizing the two phenanthrolines with potassium permanganate. Two dipyridyls are formed by the loss of two molecules of carbon dioxide (p. 942).

Hydropyridine Derivatives.

The pyridines yield hydrogen additive products, similar to those produced by benzene. They form when tin and hydrochloric acid act upon the pyridines, or more readily by the action of sodium upon the alcoholic solution; the hexa-hydro-derivatives are then the direct products. Even oxypyridines are reduced by sodium and alcohol to hexa-hydro pyridines (*Berichte*, 20, 250). Several natural alkaloids belong to this class of hydropyridines; they are especially interesting.

Hexahydro-pyridine, $C_5H_{11}N =$  $CH_2\left\langle\begin{array}{l} CH_2.CH_2 \\ CH_2.CH_2 \end{array}\right\rangle NH$, **Piperidine**, occurs attached to piperic acid as piperine (see below) in pepper. It may be artificially prepared by reducing pyridine, also by distilling the hydrochloride of pentamethylene diamine (p. 313), or by the action of sodium upon an alcoholic solution of trimethylene cyanide (p. 311).

Piperidine is a liquid that dissolves quite easily in water and alcohol. Its odor is like that of pepper. It boils at 106°. It shows a strong alkaline reaction. Its salts with the acids crystallize well. When piperidine is heated to 300° with sulphuric acid, or to 260° with nitrobenzene, or upon boiling it with silver oxide, it loses six hydrogen atoms and changes to piperidine. Nitrous acid converts it into the *nitroso* compound, $C_5H_{10}:N.NO$, boiling at 218°.

Piperidine is very reactive with brom- and iodo-benzenes, forming *n*-phenylpiperidines with them (*Berichte*, 21, 1921). This power of combination is materially diminished with α-methyl piperidine (*Berichte*, 23, 1388).

Potassium permanganate oxidizes piperidine to δ-amidovaleric and γ-amidobutyric acids. The homologous piperidines are analogously oxidized (*Berichte*, 21, 2237; 22, 1035). δ-Amidovaleric acid loses water and yields *oxypiperidine* or *piperidone*, C_5H_9ON (p. 945), a crystalline base, melting at 40° and boiling at 256°. It is a *violent poison*, resembling strychnine. The acid itself is not poisonous. *Pyrrolidon*, from γ-amido-butyric acid, is also a strychnine-like poison (*Berichte*, 23, 2772).

Dipiperidyls, $C_5H_{10}N.C_5H_{10}N$, are produced upon reducing the dipyridyls, $(C_5H_4N)_2$, with sodium and absolute alcohol (*Berichte*, 21, 2929). The same may be done with hexahydro-dipyridyls (p. 953).

Piperidine is an imide base. It contains the NH-group and can form *alkyl* and *acid* derivatives. The alkyl compounds (the hydroiodides) result by the union of piperidine with alkyl iodides.

n-**Methylpiperidine**, $C_5H_{10}N.CH_3$, and *n-Ethyl Piperidine*, $C_5H_{10}N.C_2H_5$, are alkaline liquids, boiling at 107° and 128° respectively. With methyl iodide methyl piperidine forms dimethyl piperidine ammonium iodide, $C_5H_{10}N(CH_3)_2I$. Potassium hydroxide, upon distillation with the latter, causes the decomposition of its ring structure and yields *Dimethyl piperidine*, $C_5H_9N(CH_3)_2 = CH_2:CH.CH_2.CH_2.CH_2.N(CH_3)_2$. This is a base, boiling at 118°. It reunites with methyl iodide to the ammonium iodide, $C_5H_9.N(CH_3)_3I$; silver oxide converts this into the *hydroxide*, $C_5H_9.N(CH_3)_3.OH$, which on the application of heat breaks down into trimethylamine and *Piperylene*, $C_5H_8 = CH_2:CH.CH_2.CH:CH_2$ (boiling at 42°). This is the method pursued by Hofmann in building up the piperidine bases (*Berichte*, 16, 2058; 19, 2628).

n-**Phenyl Piperidine**, $C_5H_{10}:N.C_6H_5$, from piperidine and brombenzene, is a liquid boiling about 250° (*Berichte*, 21, 2279, 2287).

n-**Acetyl Piperidine**, $C_5H_{10}N.C_2H_3O$, from piperidine by means of acetyl chloride, boils at 226°. *Benzoyl Piperidine*, $C_5H_{10}N.CO\,C_6H_5$, is a solid. *Piperidine urethanes*, $C_5H_{10}N.CO.OR$, result from the action of chlorcarbonic ester. When these acid derivatives are oxidized the piperidine nucleus is torn asunder; saturated amido acids result (*Berichte*, 17, 2544; 19, 500).

Piperine, $C_{17}H_{19}NO_3 = C_5H_{10}N.C_{12}H_9O_3$, the alkaloid, is an acid derivative of piperidine with piperic acid (p. 822). It occurs in different varieties of pepper (*e.g.*, Papaver niger). It is artificially produced by the action of piperic acid chloride upon piperidine. It crystallizes in prisms and melts at 128°. It dissolves with a deep-red color in sulphuric acid. It is a very feeble base, and is decomposed by boiling alcohol into piperidine and piperic acid.

Sodium and alcohol reduce the homologous pyridines to *homologous* piperidines. They are known as **Pipecolines**, $C_5H_9(CH_3)NH$, lupetidines, $C_5H_8(CH_3)_2NH$, etc. (Ladenburg, *Berichte*, 18, 920).

α-Methyl Piperidine, $C_5H_9(CH_3)(NH)$, α-Hydropicoline, boils at 118°.

β-**Methyl Piperidine**, β-Hydropicoline, boils at 126°. α-**Ethyl Piperidine**, $C_5H_9(C_2H_5)NH$, boils at 143°.

α-**Propyl Piperidine,** $C_5H_9(C_3H_7)NH = C_8H_{17}N$, has been obtained by the action of sodium and alcohol upon *α*-allyl pyridine (p. 944). It boils at 167°. In properties and action it is very similar to conine. Its optical inactivity alone distinguishes it from the latter. By careful crystallization of its tartrate (induced by a small crystal of conine tartrate) it may be resolved (like inactive racemic acid, p. 478) into two optically active modifications, one of which is lævo-rotatory and the other dextro-rotatory. *The latter is identical with conine*—the first synthesis of an active alkaloid (Ladenburg, *Berichte*, **19**, 2584; **22**, 1405).

Conine, $C_8H_{17}N$, dextro-rotatory *α*-normal propyl piperidine, $C_5H_9(C_3H_7)NH$, occurs in hemlock (Conium maculatum), chiefly in the seeds, and is obtained by extraction with acetic acid or distillation with soda. It is a colorless liquid, having the odor of hemlock, and boiling at 167–168°; its sp. gr. is 0.886 at 0°. It deviates the plane of polarization to the right ($\alpha_D = 13.8°$). Its hydrochloride melts at 217°.

As secondary amine it yields alkyl and acid derivatives. If its *nitrosamine*, $C_8H_{16}N(NO)$ (azoconydrine), be digested with P_2O_5 it forms *Conylene*, C_8H_{14}, boiling at 125°. **Benzoyl Conine,** $C_8H_{16}N.CO.C_6H_5$, is oxidized by permanganate of potassium to homo-coninic acid and amidovaleric acid. This nucleus is ruptured in the reaction (*Berichte*, 19, 506). Dimethyl conine iodide, $C_8H_{18}N(CH_3).CH_3I$, obtained from methyl conine and methyl-iodide, manifests the same deportment as the piperidine derivative (see above), and finally decomposes into trimethylamine and conylene, C_8H_{14}.

Conydrine, $C_8H_{17}NO$, is an oxyconine and is intimately related to conine, occurring with the latter in hemlock and in the distillation it passes over last. It crystallizes in leaflets at 120°, distils at 226°, and sublimes about 100°. It reverts to conine when heated with hydriodic acid (*Berichte*, 18, 130).

α-**Isopropyl Piperidine,** $C_5H_9(C_3H_7)NH$, is derived from *α*-isopropyl pyridine by the action of sodium and alcohol. It is very similar to conine and boils at 160°.

γ-**Phenyl Piperidine,** $C_5H_9(C_6H_5)NH$, from *γ*-phenyl piperidine, boils about 256° (*Berichte*, 20, 2590).

See *Berichte*, 23, Ref. 645 for the benzylpiperidines.

Tetrahydropyridines, $C_5H_5(H_4)N$, Piperideïnes.

α-**Methyl Piperideïne,** $C_5H_8(CH_3)N$, and *α*-**Ethyl Piperideïne,** $C_5H_8(C_2H_5)N$, have been prepared by the action of bromine and sodium hydrate upon methyl and ethyl piperidine (*Berichte*, 20, 1645).

A dipiperideïne, $C_{10}H_{18}N_2$, has been similarly derived from piperidine (*Berichte*, 22, 1322, 1377).

α-**Propyl Piperideïne,** $C_5H_8(C_3H_7)N$. The three isomeric bodies *α*-, *β*-, *γ*-coniceïns, have been obtained from conydrine, $C_8H_{17}NO$ (see above), by heating it with P_2O_5 or to 220° with hydrochloric acid, and also by the action of bromine and sodium hydrate upon conine. They are again reduced to conine when heated with hydriodic acid (*Berichte*, 23, 680 and 2141).

Paraconine, $C_8H_{15}N$, is a propyl tetrahydropyridine. It is formed from normal butyraldehyde and butylidene chloride upon heating them with alcoholic ammonia. It is a colorless liquid, with stupefying odor. It boils at 168–170° (*Berichte*, 14, 2105).

Tropine and tropidine are also tetrahydropyridine derivatives.

Tropine, $C_8H_{15}NO$, obtained by the decomposition of the alkaloid atropine, crystallizes from ether in plates, melts at 63°, and boils at 229° When heated with concentrated hydrochloric acid or with glacial acetic acid to 180°, water separates, and it yields **tropidine**, $C_8H_{13}N$, which can also be produced by heating anhydroecgonine with hydrochloric acid to 280° (*Berichte* 23, 1389). It is an oil with an odor like conine. It boils at 162°. Hydrobromic acid, acting upon it in the cold, causes it to revert to tropine. (*Berichte* 23, 1780, 2225).

Tropine is an *n-methyl-α-oxy-ethyl-tetrahydropyridine* and belongs to the *alkines* (p. 315), while tropidine is an *n*-Methyl-*α*-vinyl-tetrahydropyridine (Ladenburg, *Berichte* 20, 1648; 23, 2587):—

$C_5H_7N(CH_3).CH_2.CH_2.OH$ and $C_5H_7N(CH_3).CH:CH_2$.

Tropine. Tropidine.

Tropidine forms **hydrotropidine**, $C_8H_{15}N$, by reduction; the distillation of its hydrochloride yields methyl chloride and **Norhydrotropine**, $C_7H_{13}N$. The latter compound is isomeric with *α*-ethyl piperidine (see above) and when distilled with zinc yields *α*-ethyl pyridine, $C_5H_4N.C_2H_5$. **Anhydroecgonine**, $C_5H_7N(CH_3).CH:CH.CO_2H$, is a carboxyl derivative of tropidine; by the loss of carbon dioxide it forms tropidine.

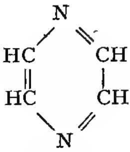
Triacetonine is closely related to tropidine (p. 209).

Nicotine, $C_{10}H_{14}N_2 = C_5H_4N.C_5H_{10}N$, is a hexahydrodipyridyl. It is found in the leaves of the tobacco plant, and may be obtained by distilling the residue from the aqueous extract with lime. It is an oil, readily soluble in water and alcohol. Its odor is very penetrating. It becomes brown in color on exposure to the air. Its specific gravity at 15° is 1.011. It boils at 241°. It is a powerful diacid base and is poisonous. Chromic acid or potassium permanganate oxidizes it to nicotinic acid. Sodium, acting upon its alcoholic solution, converts it into dipiperidyl, $C_{10}H_{20}N_2$ (p. 951).

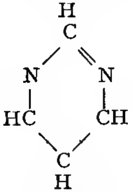
Nicotidine and **Isonicotine**, $C_{10}H_{14}N_2$, are isomeric with nicotine. They result from the reduction of *p*- and *m*-dipyridyl (p. 942) (*Berichte*, 16, 2521).

DIAZINES, OR AZINES.

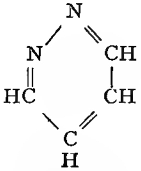
These compounds bear the same relation to pyridine, that the "five-membered" diazoles or azoles bear to pyrrol (p. 551). They contain a "six-membered" ring, consisting of four C-atoms and two N-atoms—$C_4H_4N_2$. They may be considered pyridine derivatives, in which a CH-group has been replaced by nitrogen. There are three isomeric diazine nuclei—the *orthodiazines*, *metadiazines* and *paradiazines*, corresponding to the relative position of the two N-atoms. The usual designations are *pyridazine*, *pyrimidine* and *pyrazine** :—



Paradiazine
Pyrazine.



Metadiazine
Pyrimidine.



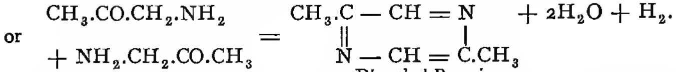
Orthodiazine
Pyridazine.

1. Paradiazine or Pyrazine Compounds.

These contain the two nitrogen atoms in the para position. They were formerly called *ketines* or *aldines* (*Berichte*, 19, 2524; 20, 431; 21, 20). They are produced by the following methods :—

1. By reducing the isonitroso ketones and isonitroso acetoacetic esters with tin and hydrochloric acid. The amido-ketone compounds formed at first sustain an immediate condensation. Thus, isonitroso acetone (p. 206) yields dimethylpyrazine (ketine) (*Berichte*, 15, 1059) :—

$$2CH_3.CO.CH(N.OH) + 6H = C_4H_2(CH_3)_2N_2 + 4H_2O,$$



$$\text{or}\quad \begin{array}{l} CH_3.CO.CH_2.NH_2 \\ + NH_2.CH_2.CO.CH_3 \end{array} = \begin{array}{l} CH_3.C - CH = N \\ \quad\| \qquad\qquad\quad | \\ \;\;N - CH = C.CH_3 \end{array} + 2H_2O + H_2.$$

Dimethyl Pyrazine.

Again, isonitrosomethyl acetone, $CH_3.CO.C(N.OH).CH_3$ (p. 209) yields tetramethyl pyrazine, $C_4(CH_3)_4N_2$ (dimethyl ketine), and isonitrosomethyl propyl ketone, $CH_3.CO.C(N.OH).C_2H_5$, gives rise to dimethyl ethyl pyrazine, $C_4(CH_3)_2(C_2H_5)_2N_2$ (diethyl ketine) (*Berichte*, 14, 1463). Dimethyl pyrazine dicarboxylic ester, $C_4(CH_3)_2N_2(CO_2)R_2$, was similarly prepared from isonitroso acetoacetic ester (*Berichte*, 15, 1051).

Tetraphenylpyrazine is obtained from benziloxime (p. 888). Isonitrosoacetophenone, $C_6H_5.CO.CH(N.OH)$ (p. 728) may be condensed to isoamidoacetophenone, $C_6H_5.CO.CH_2.NH_2$, which ammonia will convert into diphenyl pyrazine (isoindol) (*Berichte*, 21, 1278, 1947; 22, 562).

2. By the action of ammonia upon brom-keto-derivatives, R.CO.CBr.HR. Thus, brom (chlor) acetophenone, $C_6H_5.CO.CH_2Br$, yields diphenylpyrazine, $C_4H_2(C_6H_5)_2N_2$, and brom- or oxy-lævulinic acid, $CH_3CO.CHBr.CH_2.CO_2H$ (p. 344) yields tetramethyl pyrazine with the simultaneous liberation of carbon dioxide. With aniline, on the other hand, the *a*-brom ketones form indol derivatives (p. 828) (*Berichte*, 21, 123).

Pyrazines or paradiazines are diacid bases with a narcotic odor (resembling carbylamine). They are mostly liquids and volatilize quite readily with steam.

Free **Pyrazine**, $C_4H_4N_2$, appears to be produced when ammonia acts upon chloracetal, $CH_2Cl.CH(OR)_2$ (*Berichte* 21, 1481).

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* Widmann uses the terms *piazine*, *miazine*, *oiazine* (*Jour. pr. Chem.*, 38, 185). Compare Knorr, *Berichte*, 22, 2083; Hantzsch, *Annalen*, 249, 1.

Dimethyl Pyrazine, $C_4H_2(CH_3)_2N_2$, **Ketine**, from isonitrosoacetone (see above) boils with decomposition about 170–180°. **Tetramethyl Pyrazine**, $C_4(CH_3)_4N_2$, **Dimethyl Ketine**, from isonitrosomethyl acetone and from lævulinic acid, crystallizes with three molecules of water in brilliant needles. When anhydrous it melts at 86° and boils at 190°. **Diphenyl Pyrazine**, $C_4H_2(C_6H_5)_2N_2$, from bromacetophenone and amidoacetophenone, was formerly called **isoindol** (*Berichte* 21, 1279). It forms shining needles or leaflets and melts at 195°.

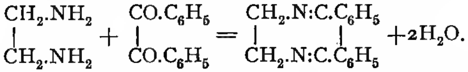
Dimethyl pyrazine Dicarboxylic Acid, $C_4(CH_3)_2N_2(CO_2H)_2$, from isonitroso-aceto-acetic ester (see above) (ketine di-carboxylic acid), is produced by oxidizing, dimethyl ethyl pyrazine with potassium permanganate (*Berichte* 20, 2524). It melts about 195° and decomposes into carbon dioxide and dimethyl pyrazine (?).

Hydropyrazines. Piperazines.

Diethylene diamine, described p. 313, may be claimed as a **hexahydropyrazine**, $C_4H_{10}N_2 = HN{<}\genfrac{}{}{0pt}{}{CH_2.CH_2}{CH_2.CH_2}{>}NH$. It sustains the same relation to pyrazine, that piperidine bears to pyridine, hence it is called *Piperazine*. Formerly it was described as a liquid boiling at 170° (*Berichte*, 23, 326). According to A. W. Hofmann it is a crystalline solid, melting at 104°, and boiling at 145-146°. Benzoyl chloride converts it into the *dibenzoyl* derivative, melting at 191° (*Berichte*, 23, 3297). It is identical with *ethylenimine* $(C_2H_4NH)_2$, which was first obtained as a carbonate, a porcelanous mass, melting at 159–163° (*Berichte*, 21, 758; 23, 3303, 3718). *Spermine* on the contrary seems to have the simple formula $C_2H_5.N$.

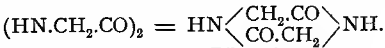
n-**Diphenyl Piperazine**, $C_6H_5.N\genfrac{}{}{0pt}{}{\diagup CH_2.CH_2 \diagdown}{\diagdown CH_2.CH_2 \diagup}N.C_6H_5$, is a *diethylene diphenyl diamine* or diethylene aniline, resulting from the interaction of ethylene bromide and aniline (*Berichte*, 22, 1387, 1778; 23, 1977). It melts at 163°.

Dihydropyrazine, $C_4H_6N_2$, derivatives are produced by the condensation of ethylene diamine with ortho diketones, just as the analogous quinoxalines and phenazines are obtained from the ortho phenylene diamines (p. 593). For example, *benzil* yields *Diphenyldihydropyrazine* (*Berichte*, 20, 267):—



$$\begin{array}{l}CH_2.NH_2\\ |\\ CH_2.NH_2\end{array} + \begin{array}{l}CO.C_6H_5\\ |\\ CO.C_6H_5\end{array} = \begin{array}{l}CH_2.N{:}C.C_6H_5\\ |\qquad\quad\ |\\ CH_2.N{:}C.C_6H_5\end{array} + 2H_2O.$$

A series of compounds which have been described as *keto-* or *azi-piperazines* are mainly amid-anhydrides of amido-acids or glycocolls (p. 368). Thus, glycine anhydride may be termed a *diketo-piperazine*:—



$$(HN.CH_2.CO)_2 = HN\genfrac{}{}{0pt}{}{\diagup CH_2.CO \diagdown}{\diagdown CO.CH_2 \diagup}NH.$$

Glycine Anhydride. Diketopiperazine.

Phenylglycin-anhydride $(C_6H_5.N.CH_2.CO)$ is

n-**Diphenyldiketopiperazine**, $C_6H_5.N\genfrac{}{}{0pt}{}{\diagup CH_2.CO \diagdown}{\diagdown CO.CH_2 \diagup}NH.C_6H_5$, etc. For different groups of similar derivatives see Abenius, *Berichte*, 21, 1664; 23, Ref. 244, and Bischof, *Berichte*, 22, 1810 and 23, 2005–2055; *Berichte*, 23, 1972.

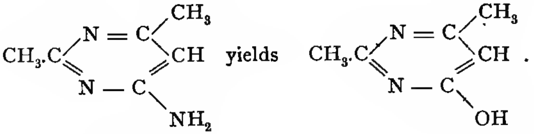
2. Metadiazines or Pyrimidine Derivatives.

These contain the two nitrogen atoms of the six-membered nucleus in the meta-position (p. 954). Thus far only amido- and oxy-derivatives have been prepared.

1. *Amido-pyrimidines* are the so-called *cyan-alkines*, formed by the polymeri-

zation of the cyan-alkyls (nitriles) when heated to 150° with metallic sodium. Thus, cyanmethane, CH_3CN, yields **cyanmethine**, $C_6H_9N_3$, cyan-ethane, C_2H_5CN, cyanethine, $C_9H_{15}N_3$, and cyan-propane, $C_3H_7.CN$, yields cyan-propine, $C_{12}H_{21}N_3$, etc.

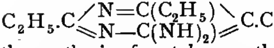
The constitution of the cyan-alkines was made evident by the fact that the oxy-base obtained by the action of nitrous acid upon cyanmethine is identical with dimethyl-oxypyrimidine (E. v. Meyer, *Jr. pr. Chem.*, 39, 265; *Berichte*, 22, Ref. 328):—



Cyan-methine.
Amido-dimethyl-
Pyrimidine.

Oxy-dimethyl-pyrimidine.

The so-called cyan-ethine (see above) is amido-diethyl-methyl-pyrimidine,



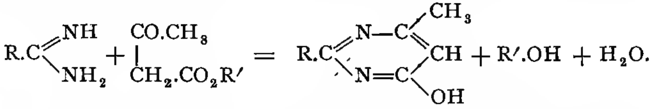
$C_2H_5.C\begin{matrix}\diagup N=C(C_2H_5)\diagdown \\ \diagdown N-C(NH)_2)\diagup\end{matrix}C.CH_3$. A confirmation of this formula is afforded by the synthesis of acetyl cyan-ethine from acetamidine, $CH_3.C(NH).NH_2$, on boiling the latter with acetic anhydride (*Berichte*, 22, 1600). Analogous cyan alkines are produced by the action of sodium upon a mixture of two alkylcyanides. The course of the reaction remains unexplained; it may be that dicyanalkyls are produced at first, and these then further combine with a cyanalkyl to form cyan-alkines (*Berichte*, 22, Ref. 327). The sodium alcoholates react in the same manner as metallic sodium (*Berichte*, 23, Ref. 630).

The *cyanalkines*, or amido-pyrimidines, are crystalline and strongly alkaline bases. They form salts with one equivalent of the acids. They are converted into oxypyrimidines by the action of nitrous acid upon heating them with hydrochloric acid to 200°.

Cyanmethine, $C_6H_9N_3$, melts at 180°. **Cyanethine**, $C_9H_{15}N_3 = C_9H_{13}N_2.NH_2$, crystallizes in white leaflets, melts at 189°, and boils with partial decomposition at 280°. The *oxy-base*, $C_9H_{13}N_2.OH$, melting at 156°, forms the *chloride*, $C_9H_{13}N_2Cl$, by the action of PCl_5. Nascent hydrogen converts the latter into *cyanconine*, $C_9H_{14}N_2$, very similar to conine. It is really methyl diethyl-pyrimidine (*Berichte*, 22, Ref. 328).

Cyan methine-ethine, $C_8H_{13}N_3$, resulting from the action of sodium upon a mixture of cyanmethane and cyanethane, consists of shining leaflets, that melt at 165°, and begin to sublime about 100°. The character of the side-chains in this compound has not yet been established. (*Jour. prk. Ch.*, 39, 267.)

(2) The **oxymetadiazines** or **oxypyrimidines** are formed when the amidines of the paraffin and benzene series act upon acetoacetic ester and analogous β ketone derivatives (the hydrochlorides are mixed in equivalent quantity with acetoacetic ester and 10 per cent. sodium hydroxide) (*Pinner*, *Berichte*, 22, 1612, 1633; 23, 3820):—



Alkyl methyl-oxy-pyrimidine.

See *Berichte*, 22, 2610 for the course of the reaction. **Alkyl oxypyrimidine** carboxylic acids are analogously derived by the use of oxalacetic ester,

$CO\left\langle\begin{matrix}CO_2R.\\ CH_2.CO_2R.\end{matrix}\right.$

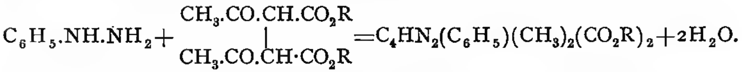
Dibasic ketonic acids, such as aceto-glutaric ester and diaceto-succinic ester, react similarly, while succino-succinic ester forms a quinazoline derivative (*Berichte*, 22, 2623; 23, 2934.)

The oxypyrimidines are crystalline substances, soluble in nearly all solvents, and form salts both with acids and bases.

Dimethyl-oxypyrimidine, $CH_3.CN_2C_3H(OH).CH_3$, forms needles that melt at 192°. **Phenylmethyl-oxypyrimidine**, $C_6H_5.CN_2C_3H(CH_3).OH$, from benzamidine, melts at 238°.

Uracyl, $C_4H_4N_2O_2$, and its derivatives, as well as malonyl urea, alloxan and the analogous carbamides, may be viewed as *keto*-derivatives of the *hydrometadiazines* (*Berichte*, 23, Ref. 643.)

(3) All compounds obtained by the condensation of phenylhydrazine (1 molecule) with diaceto-succinic ester (a γ-diketone, p. 328), appear to be *derivatives* of *ortho-diazine* or *pyridazine* in which the two N-atoms of the "six-membered" ring are adjacent (p. 954) (*Berichte*, 18, 305, 1568):—



$$C_6H_5.NH.NH_2 + \begin{matrix}CH_3.CO.CH.CO_2R\\ \vert\\ CH_3.CO.CH\cdot CO_2R\end{matrix} = C_4HN_2(C_6H_5)(CH_3)_2(CO_2R)_2 + 2H_2O.$$

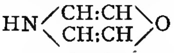
If the ester be saponified and two molecules of carbon dioxide eliminated phenyldimethylpyridazine, $C_4H_3N_2(C_6H_5)(CH_3)_2$, results. Acetophenone-acetone, $C_6H_5.CO.CH_2.CH_2.CO.CH_3$, and phenylhydrazine yield an analogous compound (*Berichte*, 17, 914).

The *benzotriazines*, $C_6H_4{:}N_3CH$, are the only known derivatives of *triazine*, $C_3H_3N_3$ (p. 553).

The osotetrazones described (p. 326) may be considered as *tetrazines*, $C_2H_4N_4$.

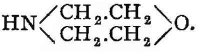
OXAZINE AND MORPHOLINE GROUP.

The oxazine ring is related in the same manner to the diazine and pyridine ring, as oxazole to diazole and pyrrol (p. 555):—



$HN\left\langle\begin{matrix}CH{:}CH\\ CH{:}CH\end{matrix}\right\rangle O$

Oxazine.

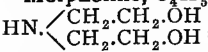


$HN\left\langle\begin{matrix}CH_2.CH_2\\ CH_2.CH_2\end{matrix}\right\rangle O.$

Morpholine.

Thus far an oxazine ring, similar to that just given, has only been shown to be present in the phen- or benzazoxines. *Tetrahydro-oxazine*, on the other hand, does exist. It is called *morpholine*; very probably because it is contained in morphine (Knorr, *Berichte*, 22, 2081).

Morpholine, C_4H_5NO, tetrahydro-oxazine, is formed when dioxyethylamine,



$HN.\left\langle\begin{matrix}CH_2.CH_2.OH\\ CH_2.CH_2.OH\end{matrix}\right.$,

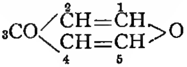
is heated to 160° with hydrochloric acid, or boiled with alkali.

n-**Methyl Morpholine**, $C_4H_4(CH_3)NO$, is similarly formed from dioxyethylmethylamine, $CH_3.N(CH_2.CH_2.OH)_2$. It is a liquid, boiling at 117°. It is very similar to methyl piperidine.

n-**Phenyl-morpholine**, $C_4H_4(C_6H_5)NO$, is obtained from dioxyethyl aniline, $C_6H_5.N(CH_2.CH_2.OH)_2$, melts at 53°, and boils at 270° (*Berichte*, 22, 2094).

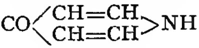
PYRONE GROUP.

The pyrone ring contains six members. It is analogous to the furfurane ring; but is less stable, owing to the influence of the CO-group, and in different reactions it readily breaks down into its components: acetone, acetic acid and oxalic acid. The conversion of most pyrone derivatives, by the action of ammonia, into derivatives of γ-pyridone (p. 945) and pyridine, is considered rather remarkable:—

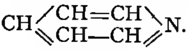


$${}_3\text{CO}\left\langle\begin{matrix}\overset{2}{\text{C}}\text{H}=\overset{1}{\text{C}}\text{H}\\ \underset{4}{\text{C}}\text{H}=\underset{5}{\text{C}}\text{H}\end{matrix}\right\rangle\text{O}$$

Pyrone.


$$\text{CO}\left\langle\begin{matrix}\text{CH}=\text{CH}\\ \text{CH}=\text{CH}\end{matrix}\right\rangle\text{NH}$$

γ-Pyridone.


$$\text{CH}\left\langle\begin{matrix}\text{CH}=\text{CH}\\ \text{CH}-\text{CH}\end{matrix}\right\rangle\text{N}.$$

Pyridine.

The following compounds are probably derivatives of the pyrone nucleus:—

Pyrone, $C_5H_4O_2$, Pyrocomane, is formed when comanic and chelidonic acids are heated to 250°. One or two molecules of carbon dioxide are eliminated (*Berichte*, 17, Ref. 423). It is a neutral solid that dissolves quite readily in water. It melts at 32.5°, and boils about 315°.

Dimethyl Pyrone, $C_5H_2O_2(CH_3)_2$ (1, 5), results upon heating dehydracetic acid (see below) with hydriodic acid. Two molecules of carbon dioxide are expelled from the acid. Brilliant crystals, that melt at 132° and boil at 248°. It sublimes at 80° in long needles. It is very soluble in water (*Berichte*, 22, 1570). Boiling baryta water converts it into diacetylacetone (p. 328), which ammonia changes to lutidone.

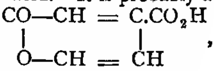
Oxypyrone, $C_5H_3O_2(OH)$ (?), pyrocomenic acid, pyromeconic acid, is obtained by the elimination of one or two groups of carbon dioxide from comenic and meconic acids by distillation. It crystallizes in large plates, melting at 121°. It boils at 228°, and even sublimes at 100°. It forms unstable salts with one equivalent of the bases (*Jour. pr. Chem.*, 27, 260).

Comanic Acid, $C_6H_4O_4 = C_5H_3O_2.CO_2H$, Pyrone Carboxylic Acid, is obtained from chelidonic acid by the loss of carbon dioxide (*Berichte*, 18, Ref. 381). It dissolves with difficulty in water. It melts at 250°, and decomposes into carbon dioxide and pyrone. When boiled with lime it decomposes into acetone, oxalic acid and formic acid. It forms an oxypicolinic acid when digested with ammonia; this breaks down into carbon dioxide and pyridone when it is heated.

Chelidonic Acid, $C_7H_4O_6 = C_5H_2O_2(CO_2H)_2$, *pyrone dicarboxylic acid*, occurs together with malic acid in *Chelidonium majus*. (Preparation, *Annalen*, 57, 274). It crystallizes in silky needles with one molecule of H_2O, and melts at 220°. It is a dibasic acid, and forms colorless salts. An excess of alkali converts it into xanthochelidonic acid, $C_7H_6O_7$. This yields yellow-colored salts with three and four equivalents of the bases; chelidonic acid is again liberated from them by the addition of acids (*Berichte*, 17, Ref. 424).

The reduction of chelidonic acid gives rise to **hydro-chelidonic acid**, $C_7H_{10}O_5$, identical with acetone diacetic acid, $CO(CH_2.CH_2.CO_2H)_2$ (p. 437; *Berichte*, 22, Ref. 681). Boiling hydriodic acid reduces chelidonic acid to α-pimelic acid (p. 421). It does not form an *acetoxime* with hydroxylamine. Ammonia converts it into an oxy-pyridine dicarboxylic acid, $C_7H_5NO_5$ (chelidamic acid, p. 948).

Coumalic Acid, $C_6H_4O_4$, is identical with comanic acid. It is probably a lactone carboxylic acid, with the following constitution,


$$\begin{matrix}\text{CO}-\text{CH} & = & \text{C.CO}_2\text{H}\\ | & & |\\ \text{O}-\text{CH} & = & \text{CH}\end{matrix},$$

and may be regarded as a carboxylic acid of α-pyrone (*Berichte*, 22, 1419, 1705).

It is produced when malic acid is heated together with concentrated sulphuric acid or with zinc chloride (p. 465) (*Berichte*, 17, 936, 2385). It dissolves with difficulty in cold water, and melts with decomposition at 206°. With an excess of alkali it forms yellow-colored salts.

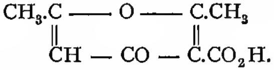
Comenic Acid, $C_6H_4O_5 = C_5H_2O_2(OH).CO_2H$, *oxypyrone carboxylic acid.* When meconic acid is heated to 120–200°, or boiled with water or hydrochloric acid, it decomposes into CO_2 and *Comenic Acid.* The latter is rather insoluble in water, and crystallizes in hard, warty masses. When digested with ammonia it changes to dioxypicolinic acid (comenamic acid, p. 947). (*Berichte*, 17, Ref. 105, 167).

Meconic Acid, $C_7H_4O_7 = C_5HO_2(OH)(CO_2H)_2$, oxypyrone dicarboxylic acid, occurs in opium in union with morphine. The opium extract is saturated with marble, and calcium meconate precipitated by calcium chloride (*Annalen*, 83, 352). The salt is afterwards decomposed by hydrochloric acid. The acid crystallizes with $3H_2O$ in white laminæ, which dissolve readily in hot water and alcohol. When heated to 120° it decomposes into carbon dioxide and comenic acid. Ferric salts color the acid solutions dark red.

In forming salts the acid generally combines with two equivalents of the bases, although with an excess of base, the salts are tribasic and yellow in color.

Meconic acid also unites with ammonia, forming *Comenamic Acid* (*Berichte*, 17, 2081).

Dehydracetic Acid, $C_8H_8O_4 =$



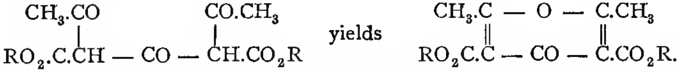
$$\begin{array}{ccccc} CH_3.C & — & O & — & C.CH_3 \\ \| & & & & \| \\ CH & — & CO & — & C.CO_2H. \end{array}$$

? (See *Berichte*, 23, Ref. 463; *Annalen*, 257, 253.)

This is a by-product in the preparation of aceto-acetic ester. It can be obtained by long continued boiling of the ester, using at the time a return condenser. It dissolves with difficulty in cold water and alcohol. It crystallizes in needles from ether; these melt at 108° and boil at 269°. Being a ketonic acid it can unite with both hydroxylamine and phenylhydrazine (*Berichte*, 18, 453).. It forms (1, 5)-dimethylpyrone on being heated with hydriodic acid.

Iso-dehydracetic Acid, $C_8H_8O_4$, is isomeric with the preceding and may be obtained by the decomposition of the condensation product, $C_{18}H_{22}O_9$ (*Annalen*, 222, 9), produced by the action of sulphuric acid upon acetoacetic ester. It is identical with *carbaceto-acetic acid* (*Berichte*, 19, 2402), derived from the aceto-acetic acid by means of hydrochloric acid. It is very probably *mesiten-lactone carboxylic acid* (*Berichte*, 23, Ref. 734).

Dimethyl Pyrone Dicarboxylic Acid, $C_9H_8O_6$ *Carbonyl Diacetic Acid.* Its ethyl ester is produced when $COCl_2$ acts upon the copper compound of aceto-acetic ester. Water is eliminated from the carbonyl diacetoacetic ester which is formed at first (*Berichte*, 19, 20):—



$$\begin{array}{lcl} CH_3.CO & & CO.CH_3 \\ \quad | & & \quad | \\ RO_2.C.CH & — CO — & CH.CO_2R \end{array} \quad \text{yields} \quad \begin{array}{lcl} CH_3.C & — O — & C.CH_3 \\ \quad \| & & \quad \| \\ RO_2C.C & — CO — & C.CO_2R. \end{array}$$

The diethyl ester is crystalline, very readily soluble in alcohol and ether, and melts at 80°. Ammonia converts it into dimethyl pyridone-dicarboxylic ester (*Berichte*, 20, 154).

2. QUINOLINE GROUP—$C_nH_{2n-11}N$.*

QUINOLINE, C_9H_7N.

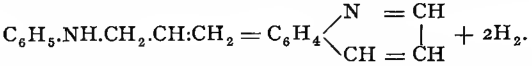
Lepidine, $C_{10}H_9N = C_9H_6(CH_3)N$—Methyl quinoline.

Cryptidine, $C_{11}H_{11}N = C_9H_5(CH_3)_2N$—Dimethyl quinoline, etc.

The quinoline bases occur with those of pyridine in bone-oil (p. 938), and are also obtained by distilling alkaloids (quinine, cinchonine, strychnine) with potassium hydroxide. The compounds *leucoline*, C_9H_7N, *iridoline*, $C_{10}H_9N$, etc., separated from coal-tar are identical with the quinoline bases (*Berichte*, 16, 1847).

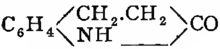
As regards synthetic methods and isomerides, quinoline is a naphthalene in which a CH-group is replaced by N (p. 937).

This was first shown by synthesizing quinoline from allyl aniline (p. 602), by passing the latter over ignited lead oxide. This is perfectly analogous to the synthesis of indol from ethyl-aniline (p. 827, and of naphthalene from phenyl butylene (p. 905) (Königs):—



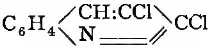
$$C_6H_5.NH.CH_2.CH{:}CH_2 = C_6H_4\left\langle\begin{matrix}N & = & CH\\ & & |\\ CH & = & CH\end{matrix}\right. + 2H_2.$$

Quinoline is also produced in the distillation of acroleïn-aniline (p. 602). A more direct proof of the constitution of quinoline was effected through its formation from hydrocarbostyril (p. 755); PCl_5 converts the latter into a dichloride, which upon heating with hydriodic acid yields quinoline (just as isatin yields indigo, p. 836) (A. Baeyer, *Berichte*, 12, 1320):—



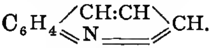
$$C_6H_4\left\langle\begin{matrix}CH_2.CH_2\\ NH\end{matrix}\right\rangle CO$$

Hydrocarbostyril.



$$C_6H_4\left\langle\begin{matrix}CH{:}CCl\\ N\end{matrix}\right\rangle CCl$$

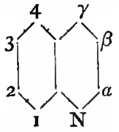
αβ-Dichlor-quinoline.



$$C_6H_4\left\langle\begin{matrix}CH{:}CH\\ N\end{matrix}\right\rangle CH.$$

Quinoline.

Here, as with naphthalene and pyridine, we represent the three replaceable hydrogen atoms of the pyridine nucleus by α, β and γ;



those of the benzene nucleus with 1, 2, 3 and 4.† The positions 1, 2, 3 correspond to the ortho-, meta-, and para-positions of the benzene derivatives. 4 corresponds to the second *meta* position (referred to N), and is known as the *Ana*-position. These posi-

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* A. Reissert, Das Chinolin und seine Derivate, 1889.

† Another nomenclature designates the affinities of the pyridine nucleus as Py-1, -2, and -3; those of the benzene nucleus as B-1, -2, -3, and -4 (*Berichte*, 17, 960).

tions are designated as the affinities of the benzene nucleus with *o*-, *m*-, *p*- and *a*-. Consequently, seven mono-derivatives of quinoline are possible (*Berichte*, 19, Ref. 443).

Of the great number of new synthetic methods of preparing quinoline and its derivatives the following are the most important:

1. The condensation of the ortho-amido-compounds of such benzene derivatives as have an oxygen atom attached to the third carbon atom of the side-chain (p. 755) (A. Baeyer).

In this way we obtain quinoline from *o*-amido-cinnamic aldehyde, *α*-methyl-quinoline from *o*-amido-cinnamic ketone, and *α*-oxy-quinoline from *o*-amido-cinnamic acid (p. 812). Further, *o*-amido-benzyl acetone yields *α*-methyl-hydro-quinoline (p. 730), *o*-amido-phenyl valeric acid, *β*-ethyl hydrocarbostyril (p. 814), and from these compounds the normal quinoline derivatives—*α*-methyl quinoline and *β*-ethyl quinoline—can be obtained by the withdrawal of 2H or O.

2. The production of quinoline and its derivatives by heating anilines (or amido-benzene compounds) with glycerol and sulphuric acid to about 190°. This method is of universal application and can be very readily executed (Skraup, *Berichte* 14, 1002):—

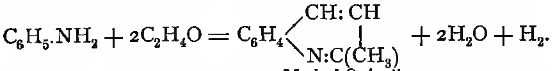
$$C_6H_5.NH_2 + C_3H_8O_3 = C_6H_4N(C_3H_3) + 3H_2O + H_2.$$

It is very probable that acroleïn first results, this then combines with the aniline derivative yielding acroleïn-aniline (see above), which is oxidized to the quinoline derivative by the elimination of two hydrogen atoms by sulphuric acid. Hence, the reaction proceeds more easily and rapidly by using a *mixture* of *aniline* with *nitrobenzene*, which only oxidizes. Similarly, from the three toluidines (and nitrotoluenes) we obtain the three methylquinolines (toluquinolines), $C_{10}H_9N = C_6H_3(CH_3)N(C_3H_3)$, from the naphthylamines (and nitronaphthalenes) the naphthoquinolines, $C_{13}H_9N$, and from the diamidobenzenes (and dinitrobenzenes) the phenanthrolines (p. 974). It is not necessary to apply the corresponding nitro-compounds together with the amido-derivatives; nitro-benzene mostly suffices as an oxidizing agent (*Berichte*, 17, 188).

Likewise, the chlor-, brom-, and nitro-quinolines result from the corresponding aniline derivatives. The nitranilines yield both nitro-quinolines and phenanthrolines (*Berichte*, 14, 2377). From the amido-sulphonic acids arise the quinoline sulphonic acids; from the amido-benzoic acids, quinoline carboxylic acids; from the amido-phenols oxyquinolines, etc.

The Kekulé benzene formula confirms the course of these quinoline syntheses (p. 563) (*Berichte*, 23, 1020).

3. An analogous reaction is the condensation of anilines with paraldehyde, aided by sulphuric or hydrochloric acid. Here *α*-methyl quinolines (quinaldines) are produced (Doebner and v. Miller):—

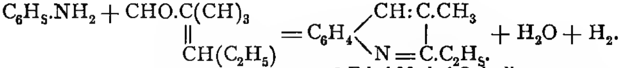


$$C_6H_5.NH_2 + 2C_2H_4O = C_6H_4\left\langle\begin{array}{l}CH:CH\\ \quad\;\;|\\ N:C(CH_3)\end{array}\right. + 2H_2O + H_2.$$

α-Methyl Quinoline.

All aldehydes of the formula $CHO.CH_2R$ react like ferric aldehyde with anilines. The first step in the reaction consists in two molecules combining to unsaturated aldehydes, CHO.CR:CH.CH_2R, or condensing to aldols corresponding to them. These then act upon the anilines and form quinoline bases.

Two aldehyde molecules always act. Their condensation is due to the influence of the CH_2 group attached to the aldehyde group. Acetaldehyde yields crotonaldehyde, CHO.CH:CH.CH_3, propyl aldehyde yields methyl ethyl acroleïn, CHO.C(CH_3):CH(C_2H_5), and ethyl propyl acroleïn is formed from normal butyraldehyde. These unsaturated aldehydes (or the aldols) then react with the anilines in such manner, that the aldehyde group attacks the benzene nucleus (and not the amido-group). Thus, α- or αβ-alkyl quinolines (*Berichte*, 17, 1713; 18, 3360) result. Acetaldehyde (crotonaldehyde) forms a methyl quinoline (see above), αβ-ethyl-methyl quinoline (*Berichte*, 21, 299) is derived from propyl aldehyde:—



αβ-Ethyl Methyl Quinoline.

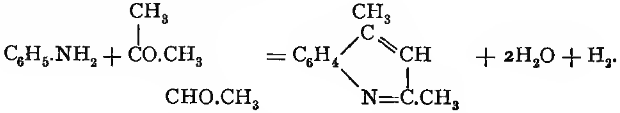
In oxidizing these dialkyl quinolines with a chromic acid mixture it is only the α-alkyl that is changed to carboxyl; the resulting carboxylic acids eliminate carbon dioxide and yield β-alkylquinolines (*Berichte*, 18, 3370).

Unsaturated aldehydes, therefore, react (with one molecule) directly with the anilines. Acroleïn (glycerol, see above) yields quinoline, while α-phenyl quinoline (*Berichte*, 16, 1664) is derived from cinnamic aldehyde, CHO.CH:CH.C_6H_5. *m*-Nitrocinnamic aldehyde reacts similarly (*Berichte*, 18, 1902).

Acetone (two molecules) reacts in the same manner as the aldehydes with aniline hydrochlorides when aided by heat. It is very probable that mesityl oxide, CH_3.CO.CH:C$(CH_3)_2$, is the first product; therefore, as there is a simultaneous splitting off of one mesityl group, the products are αγ-dimethyl quinolines (*Berichte*, 18, 3296; 19, 1394).

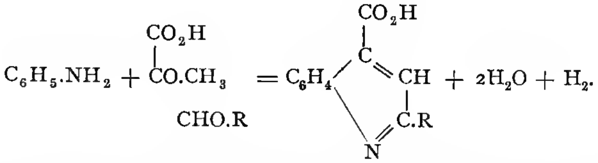
The mixture of an aldehyde and ketone (each one molecule) reacts the same as the aldehydes upon anilines. The intermediate products are unsaturated ketones, R.CO.CH:CH.R (or β-aldol ketones, R.CO.CH_2.CH(OH)R (C. Beyer, *Berichte* 20, 1767; 19, Ref. 327). In this way αγ-dialkyl quinolines are produced.

Acetone and acetaldehyde, or acetylacetone, and aniline yield αγ-dimethylquinoline (*Berichte*, 21, Ref. 138):—



The β-diketones react similarly (*Berichte*, 20, 1770; also a mixture of two different aldehydes, *Berichte*, 20, 1908, 1935).

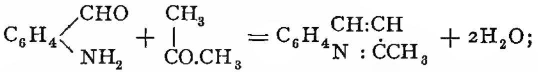
α-Alkyl-quinoline-γ-carboxylic acids are produced by the interaction of a mixture of pyroracemic acid and an aldehyde upon aniline (*Berichte*, 20, 277; 21, Ref. 12):—



The carboxylic acids lose carbon dioxide and in this manner the α-alkyl quinolines are produced. Pyroracemic acid alone when heated with aniline yields the same α-methyl quinoline-γ-carboxylic acid (aniluvitonic acid, p. 972); this is because aldehyde is formed from one molecule of the pyroracemic acid (*Berichte*, 20, 1769).

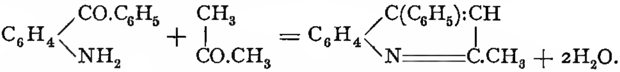
4. The direct condensation of amido-benzaldehyde with aldehydes and ketones (by the action of caustic soda). The ortho-amido-derivatives of the unsaturated homologous benzaldehydes and ketones are the first products. These immediately give up water (see p. 721) (Friedländer, *Berichte*, 16, 1833).

Thus, with acetone we get α-methyl-quinoline:—



$$C_6H_4\left<\begin{array}{l}CHO\\ NH_2\end{array}\right. + \begin{array}{l}CH_3\\ |\\ CO.CH_3\end{array} = C_6H_4\begin{array}{l}CH{:}CH\\ N\ :\dot{C}CH_3\end{array} + 2H_2O;$$

with acetophenone, $CH_3.CO.C_6H_5$, α-phenyl quinoline; with phenyl-ethyl aldehyde, $C_6H_5.CH_2.CHO$, β-phenyl quinoline; with aceto-acetic ester, α-methyl quinoline-β-carboxylic acid (*Berichte*, 16, 1833); with malonic ester α-oxyquinoline-β-carboxylic acid (*Berichte*, 17, 456). *o*-Amidobenzophenone (p. 859) reacts just like *o*-amidobenzaldehyde; it yields αγ-methyl phenyl quinoline with acetone and caustic soda (*Berichte*, 18, 2405):—

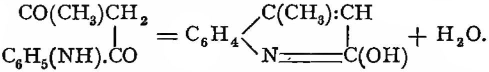


$$C_6H_4\left<\begin{array}{l}CO.C_6H_5\\ NH_2\end{array}\right. + \begin{array}{l}CH_3\\ |\\ CO.CH_3\end{array} = C_6H_4\left<\begin{array}{l}C(C_6H_5){:}CH\\ \qquad\qquad\ \ |\\ N=\!=\!=\!=C.CH_3\end{array}\right. + 2H_2O.$$

In acid solution it is only the amido group that takes part in the reaction; according to Miller's reaction benzoyl-α-methyl quinoline results.

5. The condensation of aceto-acetic esters with primary and secondary anilines (L. Knorr, *Berichte*, 17, Ref. 147; *Annalen*, 236, 112).

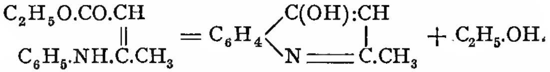
There are two phases in this reaction: (*a*) aceto-acetic anilide (from aniline and aceto-acetic ester when heated to 110°), when acted upon with concentrated acids, forms α-oxy-γ-methyl quinoline (γ-methyl carbostyril, p. 968):—



$$\begin{array}{r}CO(CH_3)CH_2\\ |\\ C_6H_5(NH).CO\end{array} = C_6H_4\left<\begin{array}{l}C(CH_3){:}CH\\ \qquad\quad\ \ |\\ N=\!=\!=\!=C(OH)\end{array}\right. + H_2O.$$

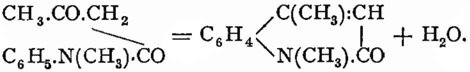
Methyl aceto-acetic anilide by the same treatment yields βγ-dimethyl carbostyril (*Berichte*, 21, Ref. 628).

(*b*) On the other hand β-phenyl-amido-crotonic ester, formed at the ordinary temperatures, yields γ-oxy-α-methyl quinoline (γ-oxyquinaldine, p. 970) when heated to 240° (Conrad and Limpach, *Berichte*, 20, 945, 1397):—



$$\begin{array}{l} C_2H_5O.CO.CH \\ \qquad\qquad\| \\ C_6H_5.NH.C.CH_3 \end{array} = C_6H_4\left\langle\begin{array}{l} C(OH):CH \\ \qquad\qquad | \\ N = C.CH_3 \end{array}\right. + C_2H_5.OH.$$

Phenyl-lutidone carboxylic ester is formed simultaneously. Anisidine, $C_6H_4(O.CH_3).NH_2$, also affords methoxy-γ-oxyquinaldine (*Berichte*, 21, 1649, 1655). Aceto-acetic ester and methylaniline condense to *n*-methyl lepidone (= pseudocarbo-styril, p. 968) (*Annalen*, 236, 105; *Berichte*, 19, Ref. 827):—

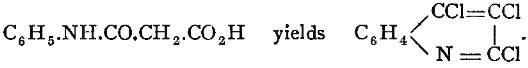


$$\begin{array}{l} CH_3.CO.CH_2 \\ \\ C_6H_5.N(CH_3).CO \end{array} = C_6H_4\left\langle\begin{array}{l} C(CH_3):CH \\ \qquad\qquad | \\ N(CH_3).CO \end{array}\right. + H_2O.$$

Acetone dicarboxylic ester (p. 435) reacts in an analogous manner with aniline (and methyl aniline); the products in this instance are esters of γ-oxyquinaldine-β-carboxylic acid (*Berichte*, 18, Ref. 469).

At the ordinary temperature benzoyl acetic ester and aniline yield β-phenylamido-phenylacrylic ester, which heated to 250° forms γ-oxy-α-phenyl quinoline (*Berichte*, 21, 521, 523).

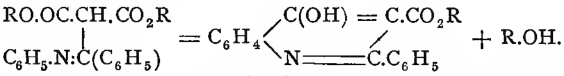
6. By the rearrangement of the aniline malonates or the malonanilides with PCl_5; triquinolines being produced (analogous to the formation of α-naphthol from phenylisocrotonic acid, Rügheimer, *Berichte*, 18, 2975):—



$$C_6H_5.NH.CO.CH_2.CO_2H \quad \text{yields} \quad C_6H_4\left\langle\begin{array}{l} CCl = CCl \\ \qquad\quad | \\ N = CCl \end{array}\right. .$$

The toludines react similarly to aniline (*Berichte*, 18, 2979), and ethyl malonic acid deports itself the same as malonic acid (*Berichte*, 20, 1235). Hippuric acid, $C_6H_5.CO.NH.CH_2.CO_2H$, under like treatment, yields chlorisoquinoline, (p. 976).

7. By rearranging the anil benzenyl compounds, from benzanilid-imide chlorides and sodium malonic or aceto-acetic ester, by the aid of heat (Just, *Berichte*, 19, 979, 1462, 1541):—



$$\begin{array}{l} RO.OC.CH.CO_2R \\ \qquad\quad | \\ C_6H_5.N:C(C_6H_5) \end{array} = C_6H_4\left\langle\begin{array}{l} C(OH) = C.CO_2R \\ \qquad\qquad\quad / \\ N = C.C_6H_5 \end{array}\right. + R.OH.$$

α-Phenyl-γ-oxy-β-quinoline carboxylic acid.

8. The conversion of indol and alkyl indols into quinolines (p. 830) is rather remarkable. It occurs in consequence of the introduction of methyl, dihydroquinolines resulting (E. Fischer, *Berichte*, 21, Ref. 17). Chlor- and brom-quinolines are similarly obtained by heating methyl ketol with chloroform or CBr_3H and sodium ethylate (*Berichte*, 21, 1940).

The quinoline bases are liquids which dissolve with difficulty in water, alcohol and ether, and possess a penetrating odor. Like pyridine they are not readily attacked by nitric or chromic acid;

potassium permanganate, however, destroys the benzene nucleus in them, with production of *αβ*-pyridine dicarboxylic acid (quinolinic acid, p. 947).

The homologous quinolines, containing the alkyl groups in the pyridine nucleus (*α*, *β*, *γ*), and those containing the substitutions in the benzene nucleus (*o*, *m*, *p*, *a*), are oxidized by chromic acid in the presence of sulphuric acid to the corresponding quinoline carboxylic acids, while potassium permanganate on the other hand usually oxidizes those substituted in the benzene nucleus, with the formation of pyridine carboxylic acids (*Berichte*, **19**, 1194; **23**, 2252).

Potassium permanganate converts the *β*- and *γ*-alkyl quinolines (by decomposing the benzene nucleus) into the corresponding pyridine tricarboxylic acids, while the *α*-alkyl quinolines have their pyridine nucleus destroyed, and acid derivatives of *o*-amidobenzoic acid result. By this treatment *α*-phenyl quinoline yields benzoyl anthranilic acid,  $C_6H_4\begin{cases}CO_2H\\NH.CO.C_6H_5\end{cases}$ (*Berichte*, 19, 1196).

If two methyl groups are present in quinoline, the *γ*-position will be oxidized with the most ease, then the *β*, and finally the *α*-position (*Berichte*, **23**, 2254).

In the case of the *αβ*-dialkylquinolines, obtained by the action of aldehydes (2 molecules) upon the anilines, chromic acid only attacks the higher *α*-alkyl with the formation of *β*-alkyl-*α*-carbonic acids (see above).

Only the most important of the many derivatives of quinoline will receive notice in the succeeding paragraphs.

Quinoline, C_9H_7N, occurs in bone oil and coal tar. It results when many alkaloids are distilled, and is best prepared synthetically.

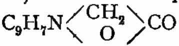
In preparing quinoline, digest a mixture of 38 grams aniline, 100 grams sulphuric acid, 24 grams nitrobenzene, and 120 grams glycerol, until the reaction commences. Boil them for several hours, dilute with water, distil off the nitrobenzene in a current of aqueous vapor, supersaturate with alkali, and distil the quinoline with aqueous vapor. To purify it thoroughly convert it into the acid sulphate (*Berichte*, 14, 1002).

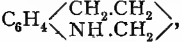
See *Berichte*, 14, 1769, for the reactions and physiological action of quinoline.

Quinoline is a colorless, strongly refracting liquid, with penetrating odor. It boils at 239°; its sp. gr. = 1.095 at 20°. It forms crystalline and very soluble salts with one equivalent of acids; the characteristic bichromate, $(C_9H_7N_2)Cr_2O_7H_2$, dissolves with difficulty and forms yellow needles, melting at 165°.

With the alkyl iodides quinoline, as tertiary base, produces crystalline, yellow ammonium iodides, which may be converted into peculiar bases (ammonium hydroxides), soluble in ether, on warming with caustic soda (*Berichte*, 17, 1953, and, 18, 410, 1015). Tertiary dihydroquinolines also afford bases soluble in ether, while the iodomethylates of tertiary tetrahydroquinolines are stable towards alkalies (*Berichte*, 21, Ref. 17). Potassium permanganate oxidizes the ammonium chlorides, the pyridine nucleus being decomposed, and derivatives of *o*-amidobenzoic acid are produced (see above).

Cyanine ($C_{29}H_{35}N_2I$) is a blue dye, and was formerly prepared by heating quinoline amyl iodide with potassium hydroxide. It is only produced in the presence of *a*-methyl quinoline (*Berichte*, 16, 1501, 1847); the same is true of the red-dye (*Berichte*, 16, 1082) obtained from quinoline with benzotrichloride.

Quinoline betaïne,  $C_9H_7N\left\langle\begin{matrix}CH_2\\O\end{matrix}\right\rangle CO$ (the HCl-salt), is formed from quinoline and chlor-acetic acid; the free betaine melts at 171°.

Nascent hydrogen (tin and hydrochloric acid) produces **Dihydro-quinoline**, C_9H_9N (melting at 161°), and liquid **Tetra-hydro-quinoline**, $C_9H_{11}N$ =  $C_6H_4\left\langle\begin{matrix}CH_2.CH_2\\NH.CH_2\end{matrix}\right\rangle$, boiling at 245° (*Berichte*, 16, 727, 23, 1142). Both are secondary bases and form nitrosamines. The tetrahydronitrosamine rearranges itself quite readily to the paranitroso compound, which yields *p* amidoquinoline when reduced (*Berichte*, 21, 862). The alkyl iodides and tetrahydroquinoline yield *n*-alkylhydroquinolines. *n*-**Methyl tetrahydroquinoline,** $C_9H_{10}N.C_2H_5$, so-called **Kairoline**, obtained by means of methyl iodide, is said to have the same action as kairine—a febrifuge.

Tetrahydroquinoline (unlike piperidine, p. 950), does not react with brombenzene. When heated with nitro-benzene it is readily oxidized to quinoline (*Berichte*, 22, 1389).

In tetrahydroquinoline the four hydrogen atoms are attached to the pyridine nucleus, therefore like the *ar*-tetrahydro naphthylamines it possesses the character of an aromatic base (of an aniline). **Decahydroquinoline,** $C_9H_{11}N$, of alicyclic character, is produced when the preceding compound is further reduced by heating with hydriodic acid. It is strongly alkaline, with a penetrating, conine-like odor. It melts at 48° and boils at 204° (*Berichte*, 23, 1142).

The **diquinolyls,** $C_9H_6N.C_9H_6N$, result from the union of two molecules of quinoline. They are analogous to the dipyridyls. They consist either of two pyridine nuclei, two benzene nuclei or one pyridine nucleus and one benzene nucleus. Seven isomerides have been prepared thus far, partly through the condensation of quinoline by sodium, or by conducting it through a tube heated to redness. Skraup has succeeded in synthesizing them from benzidine and diphenylin (p. 961), or from amidophenyl quinolines.

On heating quinoline with sodium in air we get *a*-**Diquinolyl,** melting at 176° (*Berichte*, 20, Ref. 327.) The two pyridine nuclei in it are united to each other at the *a*-positions (Py *a*-Py *a*) $C_6H_4:C_3H_2N—C_3H_2N:C_6H_4$ (*Berichte*, 19, Ref. 755; 20, Ref. 471).

The chlor-, brom-, and nitro-quinolines, with the substitutions in the benzene nucleus, are prepared synthetically, by Skraup's reaction, from the chlor-, brom-, and nitro-anilines. *a*-**Chlorquinoline,** C_9H_6ClN, is obtained from *a*-oxyquinoline with PCl_5 and PCl_3O; it consists of long needles, fusing at 38°, and boiling at 266°. It is a feeble base. Its halogen atom, in the *a*-position, is *very reactive.* When heated to 120° with water it regenerates *a*-oxyquinoline; alkyl ethers appear when it is acted upon by sodium alcoholates. It reacts in the same manner with anilines (*Berichte*, 18, 1532). See *Berichte*, 21, Ref. 232 for the action of bleaching lime upon quinoline and the chlorquinolines. Consult *Berichte*, 23, Ref. 110 upon bromquinolines

Ortho and *meta* (or *ana*)- *Nitroquinolines*, $C_9H_6(NO_2)N$, are produced when quinoline is nitrated at 80° with a mixture of nitric and sulphuric acids. The *ortho-* and *para-* have been obtained from the ortho- and paranitranilines by means of glycerol and sulphuric acid, while *m*-nitraniline yields phenanthroline (p. 974). The *ortho* melts at 89°, and the meta- (or ana-), when anhydrous, at 72°.

Amido-quinolines, $C_9H_6(H_2N)N$ (substituted in benzene nucleus), are produced in the reduction of the nitroquinolines with tin and hydrochloric acid and upon heating the oxyquinolines, $C_9H_6(OH)N$, with ammonia-zinc chloride.

1- and 4- Quinoline Sulphonic Acids (*ortho-* and *ana- Berichte*, 20, 95), are formed when quinoline is heated with fuming sulphuric acid; at 300 the *para* acid is almost the exclusive product, the ortho acid apparently being converted into this (*Berichte*, 22, 1390). *Ana* and *para-* quinoline sulphonic acids have been synthetically prepared from meta- and para amido-benzene sulphonic acid with nitrobenzene, glycerol and sulphuric acid (*Berichte*, 20, 1446).

When the three quinoline sulphonic acids (their alkali salts) are distilled with potassium cyanide in a vacuum (*Berichte*, 22, 1391), they yield the corresponding *cyanbenzquinolines*, $C_9H_6N(CN)$ (1, 3 and 4). The *ortho-* cyanide melts at 84°, the *para* (3) sublimes in needles and melts at 131°, the *ana* (4) melts at 87° (*Berichte*, 20, 1447). The cyanides can be saponified by heating them together with concentrated hydrochloric acid in a sealed tube, when they yield the corresponding quinoline benzcarboxylic acids, $C_9H_6N(CO_2H)$.

Oxyquinolines, $C_9H_6(OH)N$.

The oxyquinolines containing the hydroxyl in the benzene nucleus, called also quinophenols (1, 4, and 3, or ortho, meta, and para), are synthesized from the three amidophenols by Skraup's reaction. 1- and 4-Oxyquinolines have also been prepared from the quinoline sulphonic acids by fusion with caustic potash. They resemble the phenols and like them combine with diazo-salts forming azo-dyes (*Berichte*, 21, 1642).

1-Oxyquinoline (ortho) is also produced from 1-chlorquinoline (see above) and is most readily prepared from 1-quinoline sulphonic acid (*Berichte*, 16, 712). It crystallizes in white needles, has the odor of saffron, melts at 75°, boils at 266°, and is volatile in steam. Ferric chloride imparts a dark-green color to its alcoholic solution.

Nitrous acid converts it into *nitroso-oxyquinoline*, yellow-green needles, that by reduction yields *amido-oxyquinoline*. 1-Oxyquinoline, like the phenols and naphthols, is changed by chlorine to *chlorketoquinolines* (*Berichte*, 21, 2977).

Tin and hydrochloric acid convert it into **1-Oxytetra-hydroquinoline**, $C_9H_9(OH)NH$. This forms shining leaflets or needles, melting at 120°. It yields **oxytetra-hydro-*n*-methyl-quinoline**, $C_9H_9(OH)N.CH_3$, melting at 114°, when it is acted upon by methyl iodide. The hydrochloric acid salt of this base, $C_{10}H_{13}ON.HCl + H_2O$, is **Kairine** (*Berichte*, 16, 720), which is applied as an *antipyretic*.

3 Oxyquinoline (para), from para-amidophenol, melts at 190° (*Berichte*, 15, 893). Its *methyl ester*, *para-quinanisol*, is prepared from *p*-amidoanisol by the reaction of Skraup. It boils at 305°. Nitrous acid converts it into *o-nitroso-p-oxyquinoline*, which, upon reduction, and further oxidation by ferric chloride, forms *quinoline quinone*, $C_9H_5(O_2)N$, crystallizing in red-brown needles (*Berichte*, 21, 1887).

Tin and hydrochloric acid convert 3-oxyquinoline into *tetra-hydro-para-quinanisol*, $C_9H_{10}(O.CH_3)N$, crystallizing in stout prisms, melting at 42° and boiling at 283°. Most oxidizing agents (*e.g.* ferric chloride) color the base and its salts green. The sulphate and lactate serve as antipyretics, under the name *Thallin* (*Berichte*, 18, Ref. 613, 72.)

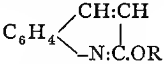
4-Oxyquinoline (ana), from para-amidophenol and from 4-quinoline sulphonic acid, crystallizes in needles or prisms, melting at 235–238° with decomposition. Ferric chloride imparts a brown-red color to its solution. Tin and hydrochloric acid convert it into a tetrahydro-compound.

The oxyquinolines, with hydroxyl in the pyridine nucleus, are more feeble bases and phenols than the oxybenzquinolines.

α-**Oxyquinoline,** $C_9H_6(OH)N$, **Carbostyril,** the lactime of *o*-amido-cinnamic acid (pp. 810, 812), is most readily obtained by digesting *o*-nitro-cinnamic ester with tin and hydrochloric acid or alcoholic ammonium sulphide (*Berichte*, **14**, 1916). It may also be prepared from *α*-chlorquinoline by heating it with water, and by digesting quinoline with a bleaching lime solution (*Berichte*, **21**, 619). It crystallizes from hot water (1 : 100) in fine needles, from alcohol in large prisms. It melts at 198–199° and sublimes.

Water decomposes its salts with alkalies and acids. Carbon dioxide separates it in the form of shining needles from its alkaline solution. Potassium permanganate oxidizes it to oxalyl anthranilic acid (p. 749). Sodium and alcohol reduce it to tetrahydroquinoline (*Berichte*, **19**, 3302). *o*-**Nitrocarbostyril** is produced when *o*-nitrocoumaric acid (p. 819) is heated together with alcoholic ammonia. It melts at 168°.

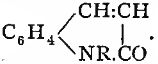
As in the case of oxypyridine or pyridone (p. 945), it is undetermined whether the lactime or lactam form should be ascribed to *α*-oxyquinoline; the ethers, however, of the two forms, of *carbostyril* and *pseudocarbostyril* exist:—



$$C_6H_4\left\langle\begin{matrix}CH:CH\\ \quad|\\ -N:C.OR\end{matrix}\right.$$

Carbostyril Ether.

and



$$C_6H_4\left\langle\begin{matrix}CH:CH\\ \quad|\\ NR.CO\end{matrix}\right. .$$

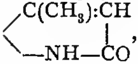
Pseudocarbostyril Ether.

The *carbostyril* or *lactime ethers*, with the group, N:C(OR), are produced by the action of the alkyl iodides upon the undecomposed (Na- or Ag-) salts of carbostyril; the *pseudocarbostyril* or *lactam ethers*, however, by the action of the alkyl iodides upon free carbostyril in the presence of alkalies (*Berichte*, **18**, 1528; **20**, 2009). The lactam ethers differ from the lactime ethers in being solid crystalline bodies, not decomposed when heated with hydrochloric acid. The *methyl ether* melts at 71°, and the ethyl at 54°.

The lactime ethers are also formed when *o*-amidocinnamic esters are digested with alcoholic zinc chloride (p. 812) and by the action of sodium alcoholates upon *α*-chlorquinolines. They are aromatic oils, that volatilize in a current of steam.

There are perfectly anologous isomeric ethers of **Hydrocarbostyril,** derived from tetrahydroquinoline, $C_9H_{11}N$.

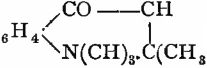
α -**Oxy-*γ*-methyl quinoline,** *γ*-**Methyl carbostyril,** or **Lepidone,** C_6H_4



$$C_6H_4\left\langle\begin{matrix}C(CH_3):CH\\ \quad|\\ -NH-CO\end{matrix}\right.$$

, from acetoacetanilide (p. 963), manifests a similar behavior. *n*-Methyl lepidone, from acetoacetic ester and methyl aniline, melts at 131°, whereas methoxy-*γ*-methyl-quinoline is a liquid (*Berichte*, **19**, Ref. 828). *γ*-*Oxy-α-methyl Quinoline*, *γ*-*Oxyquinaldine*, from phenylamidocrotonic ester (p. 963), also forms two isomeric ethers (*Berichte*, **20**, 948; **21**, 1965).

When methyl iodide acts upon γ-oxy-quinaldine, it forms an *iodomethylate*, or HI-salt, from which alkalies separate *n-methyl quinaldone*,



$C_6H_4 \begin{cases} CO \text{——} CH \\ \qquad\qquad\quad | \\ N(CH)_3.C(CH_3 \end{cases}$,

melting at 175° (*Berichte*, 22, 78). Compare lutidone.

Kynurine, β- or γ-oxy-quinoline, $C_9H_6(OH)N$, is made by heating cynurenic acid (oxyquinoline carboxylic acid, p. 973), and by oxidizing cinchonine and cinchoninic acid with chromic acid (*Berichte*, 22, Ref. 758). It crystallizes in needles, containing three molecules of water, and when anhydrous melts at 201°. It forms quinoline when heated with zinc dust. Potassium permanganate oxidizes it to oxalylanthranilic acid (cynurenic acid, p. 749). PCl_5 converts it into chlorquinoline, melting at 34°.

Dioxy-quinolines, $C_9H_5(OH)_2N$. Two isomerides have been obtained from chlorcarbostyril. A rather noteworthy formation of $\alpha\gamma$-dioxyquinoline is that from *o*-amido-phenylpropiolic acid (p. 816). Nitrous acid converts it into **trioxyquinoline, $C_9H_4(OH)_3N$**, which may be oxidized to quinisatinic acid by ferric chloride and this by loss of water yields quinisatin, $C_6H_5.NO_3$ (p. 765).

Quinoline Homologues.

The monoalkylquinolines exist in seven isomeric forms (p. 961).

(1) The seven isomeric methyl quinolines are all known.

The four quinolines *methylated in the benzene nucleus*, called **Toluquinolines, methyl benzquinolines**, or **lepidines**, are obtained by Skraup's reaction on heating the three toluidines with nitrotoluenes, glycerol and sulphuric acid. In this way *o*- and *p*-toluidine yield *o*- and *p*-methyl quinoline, while *m*-toluidine affords both the meta- and ana-quinolines. The latter can be separated by means of their acid sulphates (*Berichte*, 19, Ref. 442). The isomerism of place of the meta- and ana-compounds is obtained from the carboxylic acids, corresponding to them (p. 972). Chromic acid oxidizes all four methyl quinolines to quinoline benzcarboxylic acids; while potassium permanganate converts the four isomerides (by destruction of the benzene nucleus) into $\alpha\beta$-pyridine dicarboxylic acid (p. 947).

Ortho-methyl quinoline (1), from *o*-toluidine, boils at 248°, the *meta*- (2) boils at 250°, the *para*- (3) at 257°, and the *ana*- (4) at 250°.

The following are methylated in the pyridine nucleus:—

α-Methyl-quinoline, $C_{10}H_9N = C_6H_4{:}C_3H_2(CH_3)N$, Quinaldine, is formed in the condensation of *o*-amido-benzaldehyde with acetone when warmed with sodium hydroxide (p. 963); by the reduction of *o*-nitrobenzal acetone (p. 806); from γ-oxyquinaldine, and by fusing ethyl acetanilide with zinc chloride (*Berichte*, 23, 1903). It may also be obtained from aniline by means of ethyl aldehyde.

The most advantageous course to procure it consists in digesting 1 part of aniline with 1½ parts of paraldehyde and 2 parts crude hydrochloric acid, and then distil the product with sodium (*Berichte*, 16, 2465, 2600). As much as 25 per cent. of quinoline is found in coal-tar, but it cannot be isolated from it (*Berichte*, 16, 1082).

Quinaldine is a liquid with a faint odor resembling that of quinoline, and boils at 238°. When acted upon by potassium permanganate the pyridine ring is broken and acetyl-anthranilic acid results. Chromic acid oxidizes it to *a*-quinoline carboxylic acid.

Tin and hydrochloric acid reduces it to **Tetrahydro-quinaldine,** $C_{10}H_{13}N$, which also results by the reduction of *o*-nitrobenzyl acetone (p. 730). It boils at 247°, is a strong base, and is colored blood-red by oxidizing agents ($FeCl_3$). Alkyl iodides and quinaldine (also the lepidines) unite to iodomethylates or ammonium iodides; the caustic alkalies liberate the ammonium bases, $C_{10}H_9(NR)_2O$, from the latter (*Berichte*, 21, Ref. 14). When the iodomethylates are heated in air contact with the concentrated alkalies peculiar red and blue dyestuffs—the *Cyanines*—are produced (*Berichte*, 18, Ref. 17).

Concentrated nitric acid converts quinaldine into *o*- and *m*- **nitro-quinaldines,** $C_{10}H_8(NO_2)N$, which form *o*- and *m*-amido-quinaldine by reduction (*Berichte*, 22, 224).

γ-Oxyquinaldine and *m*-methyl-quinaldone (p. 969).

The CH_3-group of quinaldine is very reactive. It enters readily into condensation products with aldehydes (paraffin or benzene class) (*Berichte*, 20, 2041). Chloral yields the compound, $C_9H_6N.CH{:}CH.CCl_3$, melting at 144°; boiling potassium carbonate converts it into *a*-**quinoline acrylic acid,** $C_9H_6N.CH{:}CH.CO_2H$, while potassium permanganate oxidizes it to a-**quinoline aldehyde,** $C_9H_6N.CHO$. Hydrobromic acid and soda convert quinoline acrylic acid into a-**quinoline-lactic acid,** $C_9H_6N.CH(OH).CH.CO_2H$ and its *lactone* (*Berichte*, 21, Ref. 635). Consult *Berichte*, 22, 271, upon quinoline acrylic acids and quinoline aldehydes. Quinaldine and phthalic anhydride yield a beautiful yellow dye—**quinophthalone or quinoline yellow,** $C_6H_4(C_2O_2){:}CH.N.C_9H_6$ (p. 880), which may be sublimed in golden-yellow needles, melting at 235°. The sodium salt of its sulphonic acid is the **quinoline yellow** of commerce. It dyes silk and cotton a beautiful yellow.

β-**Methyl Quinoline,** $C_9H_6(CH_3)N$, is produced by heating β-methyl-a-quinoline carboxylic acid (from *a* β-ethyl-methyl quinoline, from aniline and propionic aldehyde, p. 962) and by the condensation of aniline together with propionic aldehyde and methylal (p. 962, *Berichte*, 20, 1916). It boils at 250°. It solidifies in the cold and melts at 10–14°. Chromic acid oxidizes it to β-quinoline carboxylic acid.

γ-**Methyl-quinoline,** $C_9H_6(CH_3)N$, **Lepidine,** occurs together with quinoline and quinaldine in coal-tar, and is obtained on distilling cinchonine with caustic potash. It may be synthetically prepared by the condensation of aniline with methylal (3 parts) and acetone (3 parts), aided by hydrochloric acid, by the method of v. Baeyer (p. 962). It possesses an odor like that of quinoline, and boils at 257°; it solidifies below 0°. Chromic acid oxidizes it to γ-quinoline-carboxylic acid. Potassium permanganate first produces methyl-pyridine-dicarboxylic acid, and afterwards pyridine-tricarboxylic acid ($a\beta\gamma$).

(2) Dimethyl- and Ethyl-quinolines.

$a\beta$-**Dimethyl Quinoline,** $C_9H_5(CH_3)_2N$, is obtained from a mixture of acet- and propionic aldehydes (or from tiglic aldehyde) with aniline (*Berichte*, 22, 267). $\beta\gamma$-**Dimethyl Quinoline,** from $\beta\gamma$-dimethyl-carbostyril, melts at 65° and boils at 290°. *o*- and *p*-**Oxy-**$a\gamma$-**dimethyl Quinolines,** $C_9H_4(OH)(CH_3)_2N$, have been prepared from *o*- and *p*-amidophenol with acetone (*Berichte*, 22, 209). *o*- and *p*-**Toluquinaldine,** $C_9H_5(CH_3)_2N$, containing the methylene groups in the benzene and pyridine nuclei, are obtained from *o*- and *p*-toluidine by means of paraldehyde (*Berichte*, 23, 3483). a- and β-**Ethyl Quinoline,** $C_9H_6(C_2H_5)N$, are produced (similar to the alkyl pyridines, p. 942) by heating quinoline iodoethylate to 280°

(*Berichte*, 19, 2995). β-**Ethyl Quinoline** is obtained from β-ethyl hydro-carbostyril (p. 814), just as quinoline is prepared from hydrocarbostyril (p. 961); and from β-ethyl quinoline-α-carboxylic acid (from αβ-propyl ethyl quinoline, prepared from aniline and butyraldehyde, p. 962) (*Berichte*, 18, 3371).

α-**Ethyl Quinoline** boils at 255–260°, β-**Ethyl Quinoline** at 265°, and γ-**Ethyl Quinoline** at 270–275°. These compounds yield the corresponding quinoline carboxylic acids when oxidized with a chromic acid mixture.

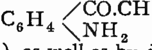
Consult *Berichte*, 21, Ref. 138 upon the *trimethyl-quinolines*.

Phenyl-quinolines, $C_9H_6(C_6H_5)N$.

α-**Phenyl-quinoline** is obtained from cinnamic aldehyde and aniline upon heating them with hydrochloric acid to 200°; also by the condensation of *o*-amidobenzaldehyde with acetophenone. It consists of brilliant needles, melting at 84°, and boiling above 300°. Potassium permanganate oxidizes it to benzoyl anthranilic acid (p. 749) (*Berichte*, 19, 1196); while tin and hydrochloric acid convert it into a tetrahydro-compound $C_9H_{10}(C_6H_5)N$. β-**Phenyl-quinoline** is produced in the condensation of *o*-amido-benzaldehyde with phenyl-acetaldehyde. It is an oil, which solidifies on cooling.

γ-**Phenyl-quinoline** is formed by heating γ-phenyl-quinaldinic acid (from γ-phenyl quinaldine, see below) to 180° (*Berichte*, 19, 2430). It crystallizes from pure alcohol in white flakes, melting at 61°, and distilling at that temperature. It apparently is the parent substance of the quinia alkaloids (*Berichte*, 20, 622).

γ-**Phenyl-α-Methyl Quinoline**, $C_9H_5(C_6H_6)(CH_3)N$, γ-phenyl quinaldine, results in the action of hydrochloric acid upon aniline mixed with acetophenone and paraldehyde (p. 961), as well as by the condensation of *o*-amido-benzophenone and acetone by means of sodium hydroxide (p. 963) (*Berichte*, 18, 2406), also by the condensation of benzoyl acetone, $C_6H_5.CO.CH_2.CO.CH_3$, with aniline, according to Beyer's method (*Berichte*, 20, 771). It melts at 99° and yields γ-phenyl quinoline-α-carboxylic acid when its phthalone is oxidized with chromic acid. This new acid affords γ-phenyl quinoline (see above).

α-**Phenyl-γ-methyl Quinoline**, $C_9H_5(C_6H_5)(CH_3)N$, is produced by condensing *o*-amido-acetophenone,  $C_6H_4\left\langle\begin{matrix}CO.CH_3\\NH_2\end{matrix}\right.$, and acetophenone with caustic soda (p. 963) (*Berichte*, 19, 1036), as well as by distilling flavenol with zinc dust. It crystallizes in white leaves and melts at 65°.

Upon heating acetanilide, $C_6H_5.NH.CO.CH_3$, with zinc chloride to 270° (by condensation of 2 molecules of the ortho-amido-acetophenone which is produced first), we obtain **Flavaniline**, $C_{16}H_{14}N_2$, applied as a beautiful yellow dye (*Berichte*, 15, 1500). It is *p*-**Amido-α-phenyl-β-methyl-quinoline**. It also results in the condensation of *o*-amido-acetophenone and *p*-amido-acetophenone when digested with zinc chloride (*Berichte*, 19, 1038). Flavaniline forms colorless crystals that become yellow on exposure to the air. Its monacid salts are yellow in color and have been used as dyes (*Berichte*, 15, 1500). Nitrous acid converts it into so-called **Flavenol**, $C_9H_5(C_6H_4OH)(CH_3)N$, a phenol, which when heated with zinc dust becomes αγ-**Phenyl-methyl-quinoline**. Potassium permanganate oxidizes flavenol to γα-methyl-quinoline-carboxylic acid (p. 972), and then to methyl pyridine tricarboxylic acid and pyridine tetracarboxylic acid.

Quinoline Carboxylic Acids,

These acids exhibit the character of amido-acids and yield salts with both bases and acids.

(1) Quinoline Monocarboxylic Acids, $C_{10}H_7NO_2 = C_9H_6N.CO_2H$.

There are four quinoline benzcarboxylic acids or those containing the carboxyl groups in the benzene nucleus. Of these the ortho, meta and para are obtained by oxidizing the corresponding methyl quinolines with chromic acid in a sulphuric acid solution. The ortho, para and ana-acids are prepared from *o*-, *p*- and *m*-amido-benzoic acids by Skraup's reaction, heating them with glycerol and sulphuric acid to 140°, further, by heating the three cyanquinolines with hydrochloric acid (p. 967).

The place-isomerism of the ana-acid (melting about 360°) is evident from its formation (together with the ortho-acid) from amido-terephthalic acid by Skraup's reaction (*Berichte*, 19, Ref. 548), from (1, 2, 3)-amidophthalic acid (together with the meta-acid) (*Berichte*, 19, Ref. 548), and from ana-quinoline sulphonic acid (p. 917) by means of the cyanide (*Berichte*, 20, 1446). The meta-acid has also been obtained by oxidizing β-di-quinolyl (*Berichte*, 19, 2473).

Ortho-Quinoline-Carboxylic Acid (1) is the most soluble in water and alcohol. It crystallizes in white needles, melting at 187°. The meta (2) acid crystallizes in needles, melting at 284–250°. The *para*-acid (3) is a white powder, and melts at about 291°, charring at the same time. The *ana*-acid (4), also prepared from meta-amido-benzoic acid, is almost insoluble in water, sublimes as a cyrstalline powder, and melts about 360° (338°) (*Annalen*, 237, 325).

The acids containing the carboxyl in the *pyridine* nucleus are prepared by oxidizing α-, β-, and γ-methyl-quinoline with chromic acid in sulphuric acid solution. Those acids, with a carboxyl in the α-position, are colored reddish-yellow by ferrous sulphate.

α-Quinoline Carboxylic Acid, $C_9H_6N(CO_2H)$, **Quinaldinic Acid**, crystallizes from hot water in needles containing $2H_2O$; it effloresces in the air, melts at 156°, and further decomposes into carbon dioxide and quinoline.

β-Quinoline Carboxylic Acid is produced by heating *Acridic acid* to 130°. It crystallizes in small plates, melts at 171°, and when oxidized with potassium permanganate yields (α, β, γ)-pyridine tricarboxylic acid (p. 949).

γ-Quinoline Carboxylic Acid, $C_9H_6N(CO_2H)$, **Cinchoninic Acid**, was first produced upon oxidizing cinchonine with potassium permanganate or nitric acid. It crystallizes in needles, containing $2H_2O$, in thick prisms, or plates with $2H_2O$ (*Berichte*, 20, 1609). It melts when anhydrous at 254°. When distilled with lime it affords quinoline; potassium permanganate oxidizes it to αβγ-pyridine tricarboxylic acid.

Methylquinoline Carboxylic Acids, $C_9H_5(CH_3)N(CO_2H)$.

γ-Methyl-α-quinoline Carboxylic Acid is obtained by oxidizing flavenol (p. 971) with potassium permanganate, and melts at 182°, with decomposition into CO_2 and γ-methyl quinoline.

α-Methyl-γ-quinoline Carboxylic Acid, α-Methyl Cinchoninic Acid, is **Aniluvitonic Acid**, obtained by the condensation of pyroracemic acid with aniline

(p. 962) (*Berichte*, 22, 1769). It crystallizes in delicate needles containing one molecule of water. It melts at 240°, and breaks down into carbon dioxide and quinaldine (*Berichte*, 14, 2249).

The homologous *α-alkyl cinchoninic acids* result in the condensation of pyroracemic acid and aldehyde with anilines (p. 962) (*Berichte*, 22, 23).

α-**Methyl-*β*-quinoline Carboxylic Acid**, $C_9H_5N(CH_3).CO_2H$ results from the condensation of *o*-amido-benzaldehyde with aceto-acetic ester (p. 962), and melts about 234°, with decomposition into carbon dioxide and quinaldine.

The **Quinaldine Carboxylic Acids** (quinaldines with carboxyl in the benzene nucleus), *α*-Methyl quinoline-carboxylic acids (ortho, meta and para), are produced by the condensation of the three amido-benzoic acids with aldehyde and hydrochloric acid.

(2) Oxyquinoline Carboxylic Acids, $C_9H_5(OH)N)CO_2H$.

α-**Oxyquinoline-*β*-Carboxylic Acid, Carbostyril-*β*-carboxylic Acid**, results in the condensation of *o*-amido benzaldehyde with malonic acid (p. 963), melts above 320°, and on heating its silver salt yields CO_2 and carbostyril.

α-**Oxyquinoline-*γ*-carboxylic Acid, Oxycinchoninic Acid**, is formed on melting cinchoninic acid with potash. It melts at 310°, and decomposes into CO_2 and carbostyril, if its silver salt be distilled.

Kynurenic Acid is also an oxy-quinoline carboxylic acid. It occurs in the urine of dogs. It consists of needles containing $1H_2O$, becomes anhydrous at 140°, and melts at 257°. Fusion with caustic potash converts it into CO_2 and kynurine.

o-**Oxy-quinoline-*m*-carboxylic Acid**, $C_9H_5(OH)N(CO_2H)$, with the hydroxyl group in the ortho position of the benzene nucleus, is produced when the sodium salt of *o*-oxyquinoline (*Berichte*, 20, 1217) is heated with CO_2 under pressure (analogous to the formation of salicylic acid):—

$$C_9H_6(ONa)N + CO_2 = C_9H_5(OH)N(CO_2Na).$$

p-Oxyquinoline by the same treatment yields *p-oxy-quinoline carboxylic acids* (*Berichte*, 20, 2695). The ortho and para acids have also been obtained from *o*- and *p*-oxyquinoline by means of CCl_4 and caustic potash (*Berichte*, 20, Ref. 564). In the same manner *o*-oxyquinaldine yields *o-oxyquinaldine carboxylic acid*, $C_9H_4(CH_3)(OH)N.CO_2H$ (*Berichte*, 21, 883).

Para-oxycinchoninic Acid, $C_9H_5(OH)N(CO_2H)(3, \gamma)$, *Xanthoquinic acid*, results on fusing parasulphocinchoninic acid (on heating cinchoninic acid to 260°, with sulphuric acid) with KOH. It crystallizes with 1 molecule of H_2O, and melts at 320° with decomposition into carbon dioxide and paraoxyquinoline. Its methyl phenol ether **Quininic Acid**, $C_9H_5(O.CH_3)N(CO_2H)$, is obtained by oxidizing quinine and quinidine with chromic acid in sulphuric acid solution, crystallizes in long, yellow prisms, dissolves in alcohol with a blue fluorescence, and melts at 280°. When heated to 230° with hydrochloric acid it decomposes into methyl chloride and para-oxycinchoninic acid.

3. *Quinoline Dicarboxylic Acids*, $C_9H_5N(CO_2H)_2$.

αβ-**Quinoline-dicarboxylic Acid**, Acridic Acid, is produced when acridine is oxidized with potassium permanganate, crystallizes in needles with $2H_2O$, or plates with $1H_2O$, and decomposes at 120–130° into CO_2 and *β*-quinoline-carboxylic acid.

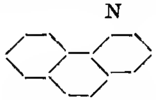
αγ-**Quinoline-dicarboxylic Acid** results when *α*-cinnamenyl-cinchoninic acid (from cinnamic aldehyde, pyroracemic acid and aniline) is oxidized with potassium permanganate. It melts with decomposition at 246° (*Berichte*, **22**, 3009).

(1, 4)-**Quinoline Dicarboxylic Acid** is obtained from amidoterephthalic acid by the action of glycerol and sulphuric acid. It crystallizes in long needles containing $2H_2O$, melts at 268–270°, and breaks down into carbon dioxide, and ortho- and ana-quinoline carboxylic acids (p. 972).

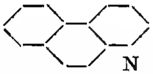
Complex Quinolines.

Just as pyridine, C_5H_5N, and quinoline, C_9H_7N, are derived from benzene, C_6H_6, and naphthalene, $C_{10}H_8$, so corresponding quinolines result from the higher, condensed benzenes.

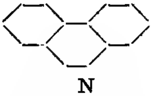
The so-called **Naphtho-quinolines**, $C_{13}H_9N$, are derived from phenanthrene by the replacement of a CH-group in a terminal benzene ring by nitrogen, whereas in phenanthridine the N-atom is present in the middle benzene nucleus:—



α-Naphtho-quinoline.



β-Naphtho-quinoline.



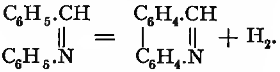
Phenanthridine.

They are produced when α- and β naphthylamines are heated with glycerol, nitrobenzene and sulphuric acid.

α-**Naphtho-quinoline** melts at 50°, and boils at 251°. β-**Naphtho-quinoline**, melts at 90°. When they are oxidized, they yield two (α- and β-) phenyl-pyridine dicarboxylic acids, $C_6H_4(CO_2H).C_5H_3N(CO_2H)$ (this is like the formation of diphenic acid from phenanthrene, p. 925), which split off two molecules of carbon dioxide and become α- and β-phenyl-pyridines (950). β-Naphtho-quinoline may also be obtained by removing bromine from α-brom-β-naphthylamine, or by the elimination of the nitro group from α-nitro-β-naphthylamine (*Berichte*, **23**, 1018).

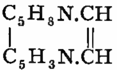
β **Naphthomethyl Quinoline**, $C_{14}H_{11}N = C_{13}H_8(CH_3)N$, β-naphthoquinaldine, is analogously produced by the action of paraldehyde and sulphuric acid upon β-naphthylamine. Potassium permanganate oxidizes it to β-naphthoquinoline carboxylic acid, $C_{13}H_8N.CO_2H$ (*Berichte*, **22**, 254; **23**, 1231).

Phenanthridine is isomeric with naphthoquinoline. In it one of the intermediate CH-groups of phenantbrene is replaced by nitrogen. It results from the pyrogenic condensation of benzylidene aniline on conducting the latter through a tube heated to redness (*Berichte*, **22**, 3339):—



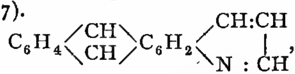
$$\begin{array}{c} C_6H_5.CH \\ \| \\ C_6H_5.N \end{array} = \begin{array}{c} C_6H_4.CH \\ |\quad\;\; \| \\ C_6H_4.N \end{array} + H_2.$$

It crystallizes in delicate white needles, melting at 104° and boiling without decomposition at 360°. Its salts are yellow in color.



Two **Phenanthrolines**, $C_{12}H_8N_2$, $= \begin{array}{c} C_5H_3N.CH \\ |\qquad\quad \| \\ C_5H_3N.CH \end{array}$, have been prepared by heating *m*- and *p*-diamidobenzene with glycerol, etc. These are derived from phenanthrene by replacement of 2 CH-groups of the terminal benzene ring by 2 nitrogen atoms (*Berichte*, **16**, 2522; **23**, 1016).

Phenanthroline, melting at 78°, is obtained from meta-nitraniline and meta-amido-quinoline by means of glycerol and sulphuric acid. Isomeric **Pseudo-phenanthroline** is also derived (in slight amount) from paranitraniline and melts at 173°. Potassium permanganate oxidizes the phenanthrolines to two dipyridyl dicarboxylic acids (*Berichte*, 19, 2377).

Anthraquinoline, $C_{17}H_{11}N$ = 
$C_6H_4\left\langle\begin{matrix}CH\\CH\end{matrix}\right\rangle C_6H_2\left\langle\begin{matrix}CH{:}CH\\ |\\ N:CH\end{matrix}\right.$, is obtained from anthramine (p. 895) on heating with glycerol, nitrobenzene and sulphuric acid. It sublimes in colorless leaflets, melts at 170°, and boils at 446°. Its solutions fluoresce very intensely. By oxidation with chromic acid in glacial acetic acid, it yields a quinone corresponding to anthraquinone; the dioxy-compound of the latter is alizarin blue.

When *m*-nitro-alizarin or amido-alizarin is heated, according to Skraup's reaction, with glycerol and sulphuric acid we obtain *alizarin-blue*, $C_{17}H_{11}NO_4$ (*Berichte*, 18, 445):—

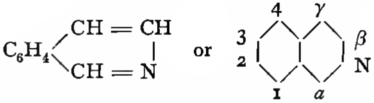
$$C_{14}H_5(O)_2(OH)_2NH_2 + C_3H_8O_3 = C_{14}H_5(O)_2(OH)_2N.C_3H_4 + 3H_2O.$$

The same occurs in trade in the form of a bluish-violet paste, and like alizarin is applied in dyeing. Since reducing agents decolorize it (zinc dust, grape sugar) and it again separates on exposure to the air, it is adapted to the vat-dyeing. It combines with sodium sulphite, yielding a compound soluble in water (same as quinoline)—the so-called *soluble alizarin-blue* (*Berichte*, 22, Ref. 368).

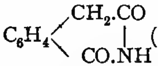
Alizarin-blue crystallizes from benzene in metallic, blue-violet needles, which melt at 270° and sublime. Heated with zinc dust it forms anthraquinoline, $C_{17}H_{11}N$ (see this); it is, therefore, a derivative of the latter, and is similarly obtained from nitroalizarin and glycerol, just as quinoline is derived from nitrobenzene and glycerol. It unites with acids and bases to form salts; those with the bases are stable.

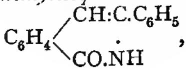
ISOQUINOLINE GROUP.

Isoquinoline is isomeric with and perfectly analogous to quinoline. Its N-atom occupies the meta-position with reference to one of the two C-atoms, which are common to both rings. It corresponds to the following scheme:—


$$C_6H_4\left\langle\begin{matrix}CH = CH\\ |\\ CH = N\end{matrix}\right. \quad \text{or}$$

This constitution seems evident from the fact that when isoquinoline is oxidized it forms cinchomeronic and phthalic acids (see below); the syntheses of the isoquinoline nucleus also argue in its favor:—

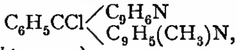
(1) By heating homophthalimide, 
$C_6H_4\left\langle\begin{matrix}CH_2.CO\\ |\\ CO.NH\end{matrix}\right.$ (p. 791) with $POCl_3$ and then reducing the resulting dichlorisoquinoline by heating it with hydriodic acid (*Berichte*, 19, 2354), or by heating homophthalimide with zinc dust (*Berichte*, 21, 2299).

In a like manner dimethyl homophthalimide (p. 791) and zinc dust yield *methylisoquinoline* (*Berichte*, 20, 1105; 21, 2300); isophthalamidine, 
$C_6H_4\left\langle\begin{matrix}CH{:}C.C_6H_5\\ \cdot\\ CO.NH\end{matrix}\right.$, forms *β-phenyl* isoquinoline (*Berichte*, 18, 3477; 19, 830);

and *o*-cyanbenzoyl cyanide is converted into *benzyl chlor- oxyisoquinoline* (*Berichte*, 21, 2679).

(2) Heating hippuric acid (p. 744) with phosphorus pentachloride and then reducing with hydriodic acid (*Berichte*, 19, 1172). This is analogous to the formation of quinoline from malonanilide (p. 964).

Isoquinoline, C_9H_7N, occurs together with quinaldine and ordinary quinoline in the crude quinoline from coal tar. It is separated from the accompanying compounds by the crystallization of the sulphates (*Berichte*, 18, Ref. 384). It is very similar to quinoline, solidifies however at 0° to a crystalline mass, melting at 20–22°, and boils at 237°. Potassium permanganate oxidizes it to phthalic acid (destroying the pyridine nucleus) and $\beta\gamma$- pyridine dicarboxylic acid (by destroying the benzene nucleus), whereas quinoline yields $\alpha\beta$- pyridine dicarboxylic acid; phthalimides, $C_6H_4(CO)_2NR$ (*Berichte*, 21, Ref. 786), result if the oxidation be moderated.

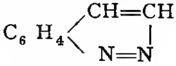
A beautiful red dye—*Quinoline Red*—is produced by condensing benzotrichloride, $C_6H_5CCl_3$, with molecular quantities of quinaldine and isoquinoline when they are heated with zinc chloride. This compound, in all probability, has a constitution,  $C_6H_5CCl\begin{matrix}\diagup C_9H_6N\\ \diagdown C_9H_5(CH_3)N,\end{matrix}$ analogous to that of malachite-green (Hofmann, *Berichte*, 20, 4).

In addition to its coloring properties, it possesses the remarkable power of rendering photographic plates orthochromatic.

β–**Phenyl isoquinoline**, $C_9H_6(C_6H_5)N$ (see above), crystallizes in leaflets, and melts at 104°.

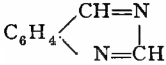
BENZO-DIAZINES.

These are analogous to the benzopyrrols (p. 826) and *benzo-diazoles* (p 571). They contain both the benzene nucleus and the diazine nucleus, with two carbon atoms in common (p. 860). They exist, in accordance with the positions of the N-atoms, in three isomeric forms:—



$$C_6H_4\begin{matrix}\diagup CH{=}CH\\ \qquad\quad |\\ \diagdown N{=}N\end{matrix}$$

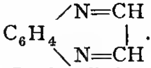
Ortho-benzdiazines
Cinnoline.



$$C_6H_4\begin{matrix}\diagup CH{=}N\\ \qquad\quad |\\ \diagdown N{=}CH\end{matrix}$$

Metabenzdiazines
Quinazoline.

and



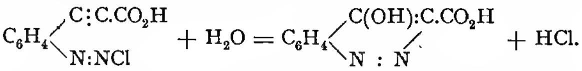
$$C_6H_4\begin{matrix}\diagup N{=}CH\\ \qquad\quad |\\ \diagdown N{=}CH\end{matrix}.$$

Parabenzdiazines.
Quinoxaline.

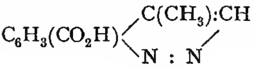
1. Cinnoline Group.

The *Cinnoline nucleus*, $C_9H_6N_2$, the first representative of the ring-chains containing two nitrogen atoms, is known in very few derivatives. It has been obtained by a closed ring being formed from the diazo-compounds; a nitrogen atom enters the side chain occupying the ortho-position.

Thus, **Oxy-cinnoline Carboxylic Acid** (v. Richter, *Berichte*, 16, 677,) is obtained from the diazo-chloride of *o*-amidophenyl propiolic acid (p. 815), when its aqueous solution is heated to 70°:—



$$C_6H_4\begin{matrix}\diagup C{:}C.CO_2H\\ \diagdown N{:}NCl\end{matrix} + H_2O = C_6H_4\begin{matrix}\diagup C(OH){:}C.CO_2H\\ \diagdown N : N\diagup\end{matrix} + HCl.$$

Methyl Cinnoline-carboxylic Acid,  $C_6H_3(CO_2H)\begin{matrix}\diagup C(CH_3){:}CH\\ \diagdown N : N\diagup\end{matrix}$ (Widmann, *Berichte*, 17, 724), is obtained in the same way, from the diazo-chloride of *o*-amido-propenyl benzoic acid (p. 778), $C_6H_3(CO_2H)\left\{\begin{array}{l}C(CH_3){:}CH\\ N_2Cl\end{array}\right.$

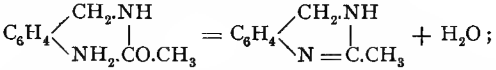
Oxycinnoline-carboxylic acid, $C_8H_4(OH)N_2(CO_2H)$, melts at 260°, with the separation of CO_2 and formation of **Oxycinnoline**, $C_8H_5(OH)N_2$, which melts at 225°, and when heated with zinc dust yields cinnoline.

o-**Phenylene-diazosulphide**, $C_6H_4\left\langle\begin{array}{c}S\\ N\end{array}\right\rangle N$ (p. 683), may be viewed as a cinnoline derivative, in which a sulphur atom replaces the group CH : CH. It sustains the same relation to cinnoline that thiophene bears to benzene or benzothiophene to naphthalene (p. 824).

2. *Quinazoline Group.*

The quinazolines contain the benzene nucleus and in addition the same ring as the pyrimidines. They are produced by analogous condensations.

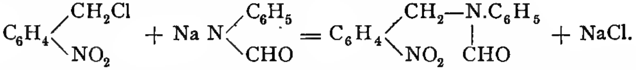
(1) Di-hydroquinazolines (and quinazolines) are obtained from the acidyl derivatives of *o*-amido benzylamine, $C_6H_4(NH_2).CH_2.NH_2$ (p. 710), by condensation, effected by mere distillation (Gabriel, *Berichte*, 23, 2808). Thus, *o*-amidobenzylacetamide yields *methyl dihydro quinazoline* :—



$$C_6H_4\left\langle\begin{array}{l}CH_2.NH\\ \qquad\ \ |\\ NH_2.CO.CH_3\end{array}\right. = C_6H_4\left\langle\begin{array}{l}CH_2.NH\\ \qquad\ \ |\\ N = C.CH_3\end{array}\right. + H_2O;$$

and *o*-amidobenzyl formamide, $C_6H_4(NH_2).CH_2.NH.CHO$, *dihydroquinazoline*, while *o*-amido benzyl benzamide forms *phenylquinazoline*, $C_6H_4\left\langle\begin{array}{l}CH = N\\ \ N = C.C_6H_5\end{array}\right.$. with simultaneous elimination of water and hydrogen.

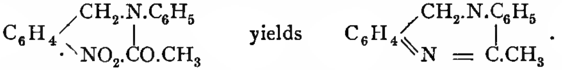
(2) Analogous acidyl compounds are produced by the action of sodium formanilides (not acetanilides) upon *o*-nitro benzyl chloride :—



$$C_6H_4\left\langle\begin{array}{l}CH_2Cl\\ NO_2\end{array}\right. + Na\,N\left\langle\begin{array}{l}C_6H_5\\ CHO\end{array}\right. = C_6H_4\left\langle\begin{array}{l}CH_2{-}N.C_6H_5\\ \qquad\quad\ |\\ NO_2\quad CHO\end{array}\right. + NaCl.$$

When these are reduced, condensation takes place, and *n*-phenyl dihydroquinazolines are produced (Paal, *Berichte*, 22, 2683).

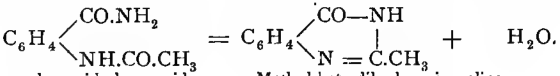
The *o* nitrobenzyl anilines yield such acidyl derivatives by the introduction of formyl and acetyl. Thus, *o*-nitro benzyl-acetanilide forms *methyl-phenyl-dihydroquinazoline* (Paal, *Berichte*, 23, 2635, Ref. 530) :—



$$C_6H_4\left\langle\begin{array}{l}CH_2.N.C_6H_5\\ \qquad\ \ |\\ NO_2.CO.CH_3\end{array}\right. \quad \text{yields} \quad C_6H_4\left\langle\begin{array}{l}CH_2.N.C_6H_5\\ \qquad\quad\ |\\ N = C.CH_3\end{array}\right. .$$

Condensation does not follow the action of nitrous acid upon the amido-benzyl anilines (*Berichte*, 23, 2188, 2636).

(3) *Keto-derivatives* of the dihydroquinazolines are obtained from *o*-amidobenzamide, $C_6H_4(NH_2).CO.NH_2$ (from anthranil carboxylic acid, p. 749, by the action of ammonia), by introducing acid radicals into it, and then condensing the resulting acidyl-amidobenzamides (Weddige, *Berichte*, 20, Ref. 630; Körner, ibid.) :—

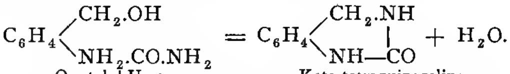


$$C_6H_4\left\langle\begin{array}{l}CO.NH_2\\ NH.CO.CH_3\end{array}\right. = C_6H_4\left\langle\begin{array}{l}CO{-}NH\\ \qquad\ |\\ N = C.CH_3\end{array}\right. + H_2O.$$

Acetyl-*o*-amido-benzamide. Methyl-keto-dihydroquinazoline.

Benzoyl-amidobenzamide under similar treatment forms phenyl-ketodihydroquinazoline.

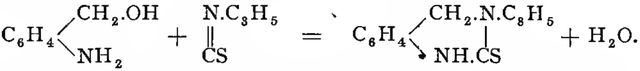
(4) Keto-derivatives of tetrahydroquinazoline are analogously obtained from *o*-amidobenzyl alcohol (p. 709) by converting it into urea derivatives (with CNK and HCl), and condensing the latter by digesting them with hydrochloric acid (Widmann, *Berichte*, 22, 1668, 2933):—



$$C_6H_4\left\langle\begin{array}{l}CH_2.OH\\ NH_2.CO.NH_2\end{array}\right. = C_6H_4\left\langle\begin{array}{l}CH_2.NH\\ \quad\;\; |\\ NH—CO\end{array}\right. + H_2O.$$

Oxytolyl Urea. Keto-tetraquinazoline.

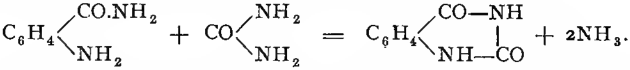
The *thioquinazolines* are prepared by digesting *o*-amido-benzyl alcohol with mustard oils:—



$$C_6H_4\left\langle\begin{array}{l}CH_2.OH\\ NH_2\end{array}\right. + \begin{array}{l}N.C_3H_5\\ \|\\ CS\end{array} = C_6H_4\left\langle\begin{array}{l}CH_2.N.C_3H_5\\ \qquad |\\ NH.CS\end{array}\right. + H_2O.$$

Mercuric oxide will convert these new compounds into ketoquinazolines.

(5) *Benzoylene Urea*, $C_8H_6N_2O_2$, is a *diketo-tetrahydro-quinazoline*. It is obtained from *o*-amido-benzamide by the action of chlorcarbonic ester, or by fusing it with urea (*Berichte*, 22, Ref. 196):—



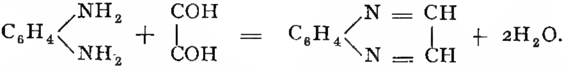
$$C_6H_4\left\langle\begin{array}{l}CO.NH_2\\ NH_2\end{array}\right. + CO\left\langle\begin{array}{l}NH_2\\ NH_2\end{array}\right. = C_6H_4\left\langle\begin{array}{l}CO—NH\\ \quad\;\; |\\ NH—CO\end{array}\right. + 2NH_3.$$

It also results in the oxidation of keto-tetrahydro-quinazoline with chromic acid (*Berichte*, 22, 2939). When heated with PCl_5 to 160° it yields dichlorquinazoline, $C_6H_4\left\langle\begin{array}{l}CCl = N\\ N = CCl\end{array}\right\rangle$, which regenerates benzoylene urea with water.

3. QUINOXALINE GROUP.

The members of this group are readily synthesized by various reactions (see Hinsberg, *Annalen*, 237, 327):—

(1) By the condensation of the orthophenylene diamines with glyoxal, COH.COH, and ortho-diketone compounds, R.CO.CO.R. This is effected by digesting their aqueous solutions (Hinsberg, *Berichte*, 17, 319; Körner, *Berichte*, 17, Ref. 573). Thus, *o*-phenylenediamine and glyoxal condense to quinoxaline, the parent substance:—



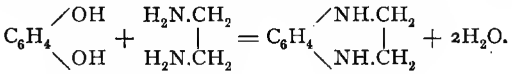
$$C_6H_4\left\langle\begin{array}{l}NH_2\\ NH_2\end{array}\right. + \begin{array}{l}COH\\ |\\ COH\end{array} = C_6H_4\left\langle\begin{array}{l}N = CH\\ \qquad\; |\\ N = CH\end{array}\right. + 2H_2O.$$

Quinoxaline.

mp-Toluylene diamine and glyoxal yield toluquinoxaline, $C_6H_3(CH_3)N_2C_2H_2$, while with benzil the product is diphenyl-toluquinoxaline, $C_6H_3(CH_3)N_2C_2(C_6H_5)_2$, and with diacetyl dimethyl toluquinoxaline (*Berichte*, 21, 1414). (1, 2, 4)-Triamido-benzene (p. 625) and glyoxal yield amido quinoxaline.

(2) The action of pyrocatechol upon ethylene diamine when heated to 200° is

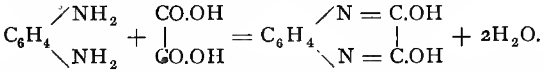
in a measure the reverse of the reaction. The product in this instance is either tetrahydroquinoxaline or ethylene-o-phenylene diamine:—



$$C_6H_4\begin{array}{l}\diagup OH\\ \\ \diagdown OH\end{array} + \begin{array}{l}H_2N.CH_2\\ \qquad\;|\\ H_2N.CH_2\end{array} = C_6H_4\begin{array}{l}\diagup NH.CH_2\\ \qquad\quad|\\ \diagdown NH.CH_2\end{array} + 2H_2O.$$

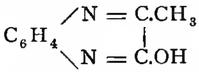
Quinoxaline is produced by oxidizing this with potassium ferricyanide (Merz, *Berichte*, 20, 1193; 21, 378).

(3) By the condensation of *o*-phenylene diamines with oxalic acid, glyoxylic acid, $COH.CO_2H$, α-ketonic acids and analogous dicarbonyl compounds, $COR.CO_2H$. Thus dioxyquinoxaline results on heating with oxalic acid to 160°:—

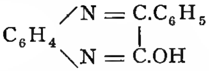


$$C_6H_4\begin{array}{l}\diagup NH_2\\ \\ \diagdown NH_2\end{array} + \begin{array}{l}CO.OH\\ |\\ CO.OH\end{array} = C_6H_4\begin{array}{l}\diagup N = C.OH\\ \qquad\quad\;|\\ \diagdown N = C.OH\end{array} + 2H_2O.$$

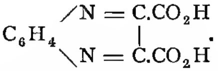
With pyroracemic acid at 60–80° the product is methyl oxyquinoxaline, with benzoyl carboxylic acid, phenyloxyquinoxaline, and with dioxytartaric acid we get quinoxaline dicarboxylic acid, etc.:—



$$C_6H_4\begin{array}{l}\diagup N = C.CH_3\\ \qquad\quad\;|\\ \diagdown N = C.OH\end{array}$$

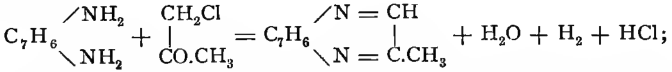


$$C_6H_4\begin{array}{l}\diagup N = C.C_6H_5\\ \qquad\quad\;|\\ \diagdown N = C.OH\end{array}$$



$$C_6H_4\begin{array}{l}\diagup N = C.CO_2H\\ \qquad\quad\;|\\ \diagdown N = C.CO_2H\end{array}.$$

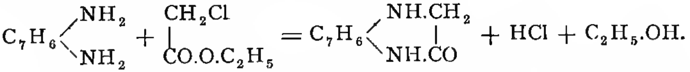
(4) The α-chlor- or brom-carbonyl compounds react just like the α-diketones and α-ketonic acids. Thus, toluylene diamine and chloracetone form methyl toluquinoxaline:—



$$C_7H_6\begin{array}{l}\diagup NH_2\\ \\ \diagdown NH_2\end{array} + \begin{array}{l}CH_2Cl\\ |\\ CO.CH_3\end{array} = C_7H_6\begin{array}{l}\diagup N = CH\\ \qquad\quad\;|\\ \diagdown N = C.CH_3\end{array} + H_2O + H_2 + HCl;$$

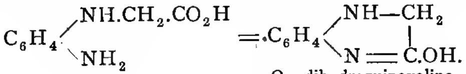
and if bromacetophenone be substituted in the reaction two isomeric phenyl toluquinoxalines, $C_7H_6 : N_2C_2H.C_6H_5$, will result, one of which may also be prepared from phenacyl nitrotoluidine (*Berichte*, 23, 166).

Keto-tetrahydro-toluquinoxaline is formed by the union of chloracetic ester with toluylene diamine (*Annalen*, 237, 360; 248, 71):—



$$C_7H_6\begin{array}{l}\diagup NH_2\\ \\ \diagdown NH_2\end{array} + \begin{array}{l}CH_2Cl\\ |\\ CO.O.C_2H_5\end{array} = C_7H_6\begin{array}{l}\diagup NH.CH_2\\ \qquad\quad|\\ \diagdown NH.CO\end{array} + HCl + C_2H_5.OH.$$

(5) An analogous reaction is the reduction of *o*-nitrophenyl- and *o*-nitrotolyl-glycocoll (p. 608) with tin and hydrochloric acid; the resulting amido-acid sustains a condensation (*Berichte*, 19, 6; 895; 20, 24; Hinsberg, *Berichte*, 22, Ref. 12):—

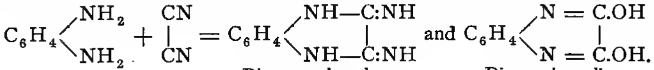


$$C_6H_4\begin{array}{l}\diagup NH.CH_2.CO_2H\\ \\ \diagdown NH_2\end{array} = C_6H_4\begin{array}{l}\diagup NH-CH_2\\ \qquad\quad\;\;|\\ \diagdown N = C.OH.\end{array}$$

Oxydihydroquinoxaline.

(6) By the action of cyanogen gas upon the orthophenylene diamines, and sub-

sequent heating of the resulting amide derivative together with hydrochloric acid to 150° (Bladin, *Berichte*, 18, 666):—



Dicyan-*o*-phenylene Diamine.

Dioxyquinoxaline.

The quinoxalines that do not contain oxygen are feeble monacid bases, generally soluble in water, alcohol and ether. Their odor resembles that of quinoline. Water decomposes nearly all their salts. The quinoxaline nucleus is quite stable in the presence of oxidizing agents, while reducing agents usually effect its decompotion. The tertiary compounds are not affected by nitrous acid. The quinoxalines result mainly by the simple interaction of their components, hence serve as a means of recognizing the ortho-diamines (p. 626), and also the orthodiketone derivatives by using *mp*-diamidotoluene, which is easily obtained (p. 626).

Quinoxaline resembles *pyrazine* (p. 954) and *phenazine* (p. 986) in that it contains two nitrogen atoms in the para position of the six-membered nucleus, and constitutes as it were a transition from the first to the latter, with which it has many analogies so far as methods of formation are concerned. Hence the three groups are all termed *diazines*, and quinoxaline is also known as *quinazine*, inasmuch as it bears the same relation to quinoline as pyrazine to pyridine. For the nomenclature of the complex azines, see *Annalen*, 237, 330; *Berichte*, 20, 23 and 327.

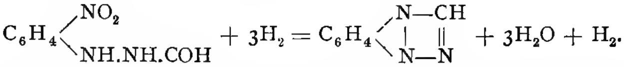
Quinoxaline, $C_8H_6N_2$, may easily be obtained from *o*-phenylene diamine and glyoxal or its compounds by digesting the aqueous solution at 60°, with sodium bisulphite. It is a crystalline mass, melting at 27° and boiling at 229° (at 760 mm.). Its odor resembles that of quinoline and piperidine. It is readily soluble even in cold water, and when heated, or by the action of alkalies, again separates from its solution. It is very soluble in acids.

Toluquinoxaline, $C_8H_6(CH_3)N_2 = C_6H_3(CH_3){:}N_2C_2H_2$, obtained from *mp*-toluylene diamine, is a colorless liquid that assumes a brown color on exposure to the air. It boils about 245°. *Methyl Toluquinoxaline*, $C_6H_3(CH_3){:}N_2.C_2H(CH_3)$, from toluylene diamine and chloracetone, is very soluble in cold water, alcohol and ether. It melts at 54° and boils about 268°. *Dimethyl Toluquinoxaline*, $C_6H_3(CH_3){:}N_2C_2(CH_3)_2$, from diacetyl and toluylene diamine, melts at 91° and boils at 270°. *Phenyl Toluquinoxaline*, $C_6H_3(CH_3){:}N_2C_2H(C_6H_5)$, from toluylene diamine and chloracetophenone, is scarcely soluble in water and melts at 135°.

Oxymethyl-toluquinoxaline, $C_6H_3(CH_3){:}N_2C_2\genfrac{}{}{0pt}{}{\diagup CH^3}{\diagdown OH}$, is derived from toluylene diamine and pyroracemic acid (p. 979). It sublimes in colorless needles, melting at 220°. It dissolves in water with difficulty. It forms colorless solutions with the alkalies, and with the acids yellow-colored liquids. **Oxy-phenyltoluquinoxaline**, $C_6H_3(CH_3){:}N_2C_2\genfrac{}{}{0pt}{}{\diagup C_6H^5}{\diagdown OH}$, from toluylene diamine and phenylglyoxylic acid, crystallizes in yellow needles, that sublime and become white, melting at 196°. The alkali solutions are colorless, those with acids are yellow in color.

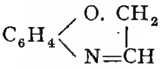
Dioxytoluquinoxaline, $C_6H_3(CH_3):N_2C_2\left\langle\begin{matrix}OH\\OH\end{matrix}\right.$, results upon heating toluylene diamine together with oxalic acid, as well as from dicyantoluylene diamine (see above) (*Annalen*, 237, 348). It dissolves with difficulty in water, forms white needles, and melts above 300°. It forms salts with bases; water, however, decomposes them.

Benzotriazines (p. 957) may be obtained from *o*-nitrophenylhydrazine by reducing its acidyl derivatives with zinc dust or sodium amalgam. *Benzo-triazine* is thus prepared from formyl nitrophenylhydrazine (*Berichte*, 22, 2806) :—



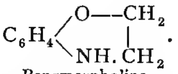
Methyl benzotriazine is similarly derived from the acetyl compound. The benzotriazines are yellow, crystalline compounds, with a peculiar odor resembling that of the alkaloids. They are feeble bases. Benzotriazine, $C_7H_5N_3$, melts at 65° and boils at 235–240°. Methyl benzotriazine, $C_7H_4.(CH_3)N_3$, melts at 89° and boils at 250–255°.

Benzoxazines (p. 957).



Benzoxazine.

and



Benzmorpholine.

Phenyl benzoxazine, $C_8H_6(C_6H_5)NO$, is obtained from *o*-nitrophenol-phenacyl ether, $C_6H_4(NO_2).O.CH_2.CO.C_6H_5$ (from *o*-nitrophenol and bromacetophenone), by reduction with stannous chloride and hydrochloric acid. It melts at 103° and is a feeble base (*Berichte*, 23, 172).

Benzomorpholine, C_8H_9NO, **Phenmorpholine** (see above), may be prepared by heating oxyethyl-*o*-amidophenol, $C_6H_4(NH_2)O.C_2H_4.OH$ (from amidine) with hydrochloric acid and then with sodium hydroxide (p. 957). It is a colorless oil, with a characteristic odor. It boils at 268°.

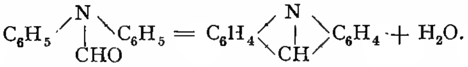
Methyl Benzomorpholine, $C_8H_8(CH_3)NO$, from methyl anisidine, boils at 261° (*Berichte*, 22, 2098).

THE ACRIDINE GROUP.

The parent substance **acridine**, $C_{13}H_9N$, is an analogue of *pyridine* and *quinoline*. It is an anthracene, in which N replaces an intermediate CH-group of normal anthracene. The third affinity of the nitrogen atom is combined with the opposite carbon atom (p. 894). The acridines may be synthesized :

(1) From diphenylamine, and the fatty acids, or from the acid

derivatives of diphenylamine, if they be heated together with zinc chloride (Bernthsen, *Annalen*, **224**, 1; *Berichte*, **16**, 1820):—

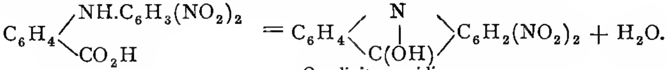


$$C_6H_5\text{—}N(CHO)\text{—}C_6H_5 = C_6H_4\left\langle{N \atop CH}\right\rangle C_6H_4 + H_2O.$$

Formyl Diphenylamine. Acridine.

Homologous acridines are similarly obtained from diphenylamine and the higher fatty acids. In them the hydrogen of the CH-group is replaced by alkyls. They are called meso-derivatives (*Berichte*, 18, 690). *ms*-Methyl acridines are similarly formed when *p* phenyl tolylamine, $C_6H_5.NH.C_8H_4.CH_8$ (p. 624), is heated together with acids and zinc chloride (*Berichte*, 20, Ref. 376).

(2) An analogous reaction is the rearrangement of dinitro diphenylamine *o*-carboxylic acid (from chlordinitrobenzene and *o*-amidobenzoic acid) when heated with sulphuric acid, or if reduced with tin and hydrochloric acid, a diamido-derivative being thus produced (*Berichte*, 8, 1444):—



$$C_6H_4\left\langle{NH.C_6H_3(NO_2)_2 \atop CO_2H}\right. = C_6H_4\left\langle{N \atop C(OH)}\right\rangle C_6H_2(NO_2)_2 + H_2O.$$

Oxydinitro-acridine.

The acridines are feeble bases; their salts are decomposed by boiling water. The oxidation of acridine with potassium permanganate affords (through the destruction of a benzene nucleus) $\alpha\beta$-quinoline dicarboxylic acid (p. 973).

Acridine has also been obtained from ortho-tolylaniline, $C_6H_5.NH.C_6H_4.CH_3$, by conducting the vapors through a red-hot tube (analogous to the synthesis of anthracene); by heating diphenylamine with chloroform and zinc chloride to 200°, and when aniline and salicylic aldehyde are heated to 260° with zinc chloride (*Berichte*, 12, 2452). It is very soluble in alcohol and ether. It occurs in crude anthracene and dissolves in dilute acids with a beautiful green fluorescence. It readily sublimes in colorless leaflets, sublimes at 100°, melts at 110°, distils above 360°, and has a very pungent odor.

Dihydroacridine, $C_6H_4\left\langle{CH_2 \atop NH}\right\rangle C_6H_4$, is formed when acridine is reduced with sodium amalgam or zinc and hydrochloric acid. It no longer manifests basic properties and melts at 168°. Oxidizing agents, even silver nitrate, convert it again into acridine.

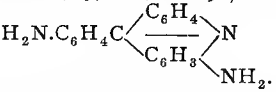
The acridines yield iodides with the alcoholic iodides. Silver oxide or alkalies convert them into peculiar ammonium bases which are very similar to the quinoline compounds (p. 965). Potassium permanganate attacks the pyridine nucleus present in these alkyl iodide derivatives, forming then phenyl-*o*-amidobenzoic acid, $C_6H_5.NH.C_6H_4.CO_2H$ (*Berichte*, 18, 2709).

***ms*-Methyl Acridine**, $C_{13}H_8(CH_3)N$ (see above), is formed when diphenylamine and glacial acetic acid are heated together with zinc chloride to 220°. It consists of colorless plates, melting at 114°. Its hydrochloride crystallizes in yellow leaflets, that dissolve with a bluish-green fluorescence. Chloral and methyl acridine unite to the compound, $C_{13}H_8N.CH_2CH(OH).CCl_3$, which yields **acridylacrylic acid**, $C_{18}H_8N.CH : CH.CO_2H$, when digested with caustic soda. Potassium permanganate oxidizes this compound to ***ms*-acridylaldehyde**, $C_{18}H_8N.CHO$, and ***ms*-acridyl carboxylic acid**, $C_{13}H_8N(CO_2H)$ (*Berichte*, 20, 1541).

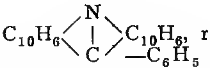
***ms*-Phenyl Acridine**, $C_{18}H_8(C_6H_5)N$, results upon heating diphenylamine and benzoic acid together with zinc chloride to 260°. It crystallizes in yellow plates (from benzene, with one molecule of benzene), melts at 181° and distils above

400°. Its salts are yellow in color, and are decomposed by water. *p*-Amido- and *p*-oxy diphenylamine together with benzoic acid yield the corresponding phenylamidoacridine and phenyl oxyacridine (*Berichte*, 28, 692).

Chrysaniline, $C_{19}H_{11}N(NH_2)_2$. This is obtained as a by-product in the rosaniline manufacture. On mixing the mother liquors with nitric acid the nitrate separates; this is the chief constituent of the beautiful yellow dye *phosphine*. Free chrysaniline crystallizes from dilute alcohol in golden yellow needles, melting about 268°. It forms red colored salts with the acids (1 equivalent); these dye silk and wool a beautiful yellow. Their solutions exhibit a beautiful yellow-green fluorescence.

Chrysaniline has been prepared synthetically by the oxidation of ortholeucaniline with arsenic acid (*Berichte*, 17, 208; 18, 696). It is therefore **p-amido-phenyl-2-amido acridine**,  $H_2N.C_6H_4C{<}\genfrac{}{}{0pt}{}{C_6H_4}{C_6H_3}{>}N$, $-NH_2$.

When chrysaniline is diazotized and boiled with alcohol, it yields *ms*-phenylacridine. If heated to 180° with hydrochloric acid, an amido-group splits off and *Chrysophenol*, $C_{19}H_{11}(OH)N.NH_2$, is produced.

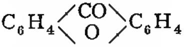
Phenyl-β-naphthyl Acridine,  $C_{10}H_6{<}\genfrac{}{}{0pt}{}{N}{C-C_6H_5}{>}C_{10}H_6$, results upon heating β-dinaphthylamine, $(C_{10}H_7)_2NH$, and benzoic acid to 240°, together with zinc chloride. It melts at 297°.

Consult *Berichte*, 18, 691, upon the nomenclature of the complex acridines.

Thiodiphenylamine (p. 604), diphenylene keton-oxide or *xanthone* (p. 860), and thioxanthone are analogous to acridine in constitution. They all possess a strong *chromogenic* character:—


$C_6H_4{<}\genfrac{}{}{0pt}{}{NH}{S}{>}C_6H_4$

Thiodiphenylamine.


$C_6H_4{<}\genfrac{}{}{0pt}{}{CO}{O}{>}C_6H_4$

Xanthone.


$C_6H_4{<}\genfrac{}{}{0pt}{}{CO}{S}{>}C_6H_4$.

Thioxanthone.

Thioxanthone, $C_{13}H_8SO$, is produced in the condensation of diphenylsulphide-*o*-carboxylic acid, $C_6H_5S.C_6H_4.CO_2H$ (from thiophenol and diazoanthranilic acid, see phenyl sulphide (p. 672), effected by sulphuric acid. It consists of yellow needles, that become colorless upon distillation. It melts at 207° and boils at 372° (*Berichte*, 23, 2469).

Phenoxazine,  $C_6H_4{<}\genfrac{}{}{0pt}{}{NH}{O}{>}C_6H_4$, or phenazoxine (see *Berichte*, 22, 2081), is also analogous to acridine and thiodiphenylamine. It is obtained similarly to thiodiphenylamine and phenazine (see below), when *o*-amidophenol is heated together with pyrocatechol to 260–280°. It crystallizes from dilute alcohol in leaflets, that melt at 148°, and sublime. In its reactions it is very similar to thiodiphenylamine, and it is only in its oxidation product that it shows a *chromogenic* character (Nietzki, *Berichte*, 22, 3036). A reddish-violet dye (*Berichte*, 20, 942) is produced by nitration, reduction of the nitro product with tin and hydrochloric acid, and again oxidizing with ferric chloride (analogous to the formation of Lauth's violet from thiodiphenylamine, p. 605).

Resorufin and *resazurine*, products obtained from resorcinol, appear to be derivatives of phenoxazine (p. 691).

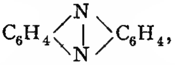
The *Oxyindamines* and *oxindophenols*, so called by Nietzki (Organische Farbstoffe, 1889, p. 139; *Berichte*, 21, 1736), are dyestuffs and appear to be phenoxazine derivatives. They result upon digesting nitroso-dimethyl aniline or quinone dichlorimide with β-naphthol. They differ from the indophenols, which are produced when the reaction occurs at low temperatures, in that the two benzene nuclei are united a second time by means of oxygen, and hence possess a constitution analogous to that of the thiodiphenylamine derivatives and the eurhodines. Gallocyanine and naphthol violet belong in this series.

Gallocyanine, $C_{15}H_{12}N_2O_5$ (Violet solide von Koechlin), is produced by the action of nitroso-dimethyl aniline upon gallic acid, catechuic acid, etc. It forms shining green needles and serves as a beautiful violet-colored lake in calico printing (*Berichte*, 21, 1740). *Naphthol Violet*, $C_{18}H_{14}N_2O$, of Meldola and Witt, β-Naphthol Blue, New Blue, Fast Blue, Cotton Blue, results upon heating nitroso-dimethyl aniline and β-naphthol. Its hydrochloride consists of bronze-colored needles. It dyes cotton, that has been mordanted with tannin, violet blue, similar to indigo (*Berichte*, 21, 1744; 23, 2247).

When the free bases of these dyes are heated they become insoluble in ether, and change to peculiar green-blue dyes that O. Witt has named *cyanamines*, (*Berichte*, 23, 2249).

PHENAZINE GROUP.

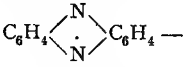
The simplest parent substance in this group is *phenazine*, $C_{12}H_8N_2$. In constitution it is analogous to anthracene and acridine. In it the two intermediate C-atoms of anthracene are replaced by two nitrogen atoms:—



$$C_6H_4{<}\overset{N}{\underset{N}{|}}{>}C_6H_4$$

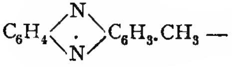
, Phenazine.

It contains in addition to the two terminal benzene rings an intermediate ring-chain, consisting of four C-atoms and two nitrogen atoms; this is similar to the paradiazine or pyrazine ring. The constitution and nomenclature of the more complex azines may be seen from the following arrangement (*Berichte*, 20, 23, 327; *Annalen*, 237, 330):—



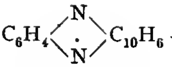
$$C_6H_4{<}\overset{N}{\underset{N}{\cdot}}{>}C_6H_4$$

— Phenazine or Diphenazine.

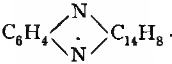


$$C_6H_4{<}\overset{N}{\underset{N}{\cdot}}{>}C_6H_3.CH_3$$

— Methylphenazine or Toluphenazine.



$C_6H_4\left\langle\begin{matrix}N\\ \cdot\\ N\end{matrix}\right\rangle C_{10}H_6$ — Naphthophenazine or Phenonaphthazine.

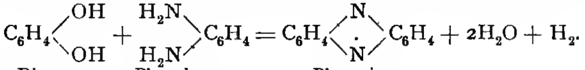


$C_6H_4\left\langle\begin{matrix}N\\ \cdot\\ N\end{matrix}\right\rangle C_{14}H_8$ — Anthraphenazine or Phenanthrazine.

$C_{10}H_6\left\langle\begin{matrix}N\\ \cdot\\ N\end{matrix}\right\rangle C_{10}H_6$ — Naphthazine or Dinaphthazine, etc.

The following are the most important methods in use for the preparation of the azines:

1. Condensation of ortho-phenylenediamine (p. 629) with ortho-dioxybenzenes, *e.g.*, pyrocatechin, when heated to 200° (Merz and Ris, *Berichte*, 19, 726, 2206):—

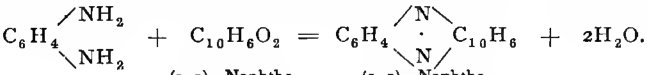


$$C_6H_4\left\langle\begin{matrix}OH\\ OH\end{matrix}\right. + \left.\begin{matrix}H_2N\\ H_2N\end{matrix}\right\rangle C_6H_4 = C_6H_4\left\langle\begin{matrix}N\\ \cdot\\ N\end{matrix}\right\rangle C_6H_4 + 2H_2O + H_2.$$

(1,2)—Dioxy-benzene   *o*-Phenylene diamine.   Phenazine.

Pyrocatechine and *mp*-toluylene diamine (p. 626), in a similar manner yield methyl-phenazine or tolu-phenazine (see above).

2. Condensation of the ortho diamines with ortho diketones, or orthoquinones, *e.g.*, β-naphthoquinone—a reaction, perfectly analogous to the formation of the quinoxalines (p. 979) (Hinsberg, *Annalen*, 237, 329).

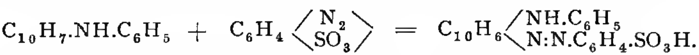


$$C_6H_4\left\langle\begin{matrix}NH_2\\ NH_2\end{matrix}\right. + C_{10}H_6O_2 = C_6H_4\left\langle\begin{matrix}N\\ \cdot\\ N\end{matrix}\right\rangle C_{10}H_6 + 2H_2O.$$

(1, 2)—Naphtho-quinone.   (1, 2)—Naphtho-phenazine.

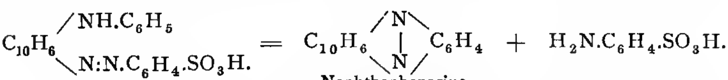
Similarly *o*-toluylene-diamine yields with phenanthraquinone toluanthrazine, β-naphtho-quinone, tolu-naphthazine, with isatine tolu-indazine, $C_7H_6(N_2)C_8H_5N$, while *o*-naphthylene diamine and β-naphthoquinone yield di-naphthazine, etc.

3. A very convenient method is the conjugation of phenyl—(tolyl, etc.)—β-naphthylamine (p. 911) with diazobenzene sulphonic acids; the diazo group enters the ortho-position of the naphthylamine and azo-compounds result at first:—



$$C_{10}H_7.NH.C_6H_5 + C_6H_4\left\langle\begin{matrix}N_2\\ SO_3\end{matrix}\right\rangle = C_{10}H_6\left\langle\begin{matrix}NH.C_6H_5\\ N{:}N.C_6H_4.SO_3H.\end{matrix}\right.$$

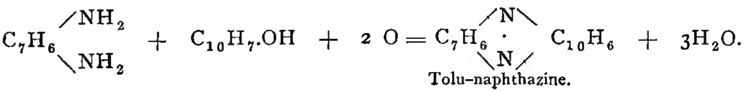
Boiling dilute acids change the azo-derivatives to azines and sulphanilic acid (Witt, *Berichte* 20, 571):—



$$C_{10}H_6\left\langle\begin{matrix}NH.C_6H_5\\ N{:}N.C_6H_4.SO_3H.\end{matrix}\right. = C_{10}H_6\left\langle\begin{matrix}N\\ |\\ N\end{matrix}\right\rangle C_6H_4 + H_2N.C_6H_4.SO_3H.$$

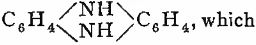
Naphthophenazine.

4. The oxidation of an orthophenylene diamine, together with β-naphthol (Witt, *Berichte*, 19, 914; 20, 575):—



$$C_7H_6\left\langle\begin{matrix}NH_2\\ NH_2\end{matrix}\right. + C_{10}H_7.OH + 2\ O = C_7H_6\left\langle\begin{matrix}N\\ \cdot\\ N\end{matrix}\right\rangle C_{10}H_6 + 3H_2O.$$

Tolu-naphthazine.

The azines are mostly yellow-colored, feebly basic bodies that cannot be distilled without suffering decomposition. They dissolve in concentrated sulphuric acid with a red to blue color. They are again precipitated upon addition of water, the liquid becoming yellow in color in consequence. Ammonium sulphide reduces them to colorless, dihydro-compounds,  $C_6H_4\left\langle{NH \atop NH}\right\rangle C_6H_4$, which are readily re-oxidized to azines.

Phenazine, $C_{12}H_8N_2$, was first obtained from azo benzoates by distillation, and was called *Azodiphenylene* (p. 847). It may also be prepared from *o*-phenylene diamine and pyrocatechin, and by conducting aniline vapors through a tube heated to redness (*Berichte*, 19, 420, 3256). It crystallizes and sublimes in bright-yellow needles, melting at 171°. It dissolves in concentrated sulphuric acid with a blood-red color, which becomes yellow upon the addition of water (*Berichte*, 19, 2207).

Methyl Phenazine, $C_{12}H_7(CH_3)N_2$, *Toluphenazine*, from pyrocatechol and *o*-toluylene diamine (see above), consists of yellow needles, melting at 117° and dissolving in dilute acids (*Berichte*, 19, 726).

Naphthophenazine, $C_6H_4(N)_2C_{10}H_6$, may be readily prepared from phenyl naphthylamine. It forms yellow needles, that melt at 142° and sublime about 200°. It dissolves in concentrated sulphuric acid with a brownish-red color (*Berichte*, 20, 573, 2660). *Nitro-naphthophenazine*, $C_6H_4(N_2)C_{10}H_5(NO_2)$, from nitro-$\beta$-naphthoquinone and *o*-phenylene diamine, melts at 221° (*Berichte*, 23, 175).

Tolu-naphthazines, $C_7H_6(N_2)C_{10}H_6$. There are four possible isomerides; three of these are known. Two are produced by the condensation of *o*-toluylene diamine with β-naphthoquinone, and a third has been obtained by the decomposition of wool-black (*Berichte*, 20, 577).

Pheno- and Tolu-anthrazine, $C_6H_4(N_2)C_{14}H_8$, and $C_7H_6(N_2)C_{14}H_8$, are easily formed on mixing the warm solution of phenanthraquinone in glacial acetic acid with the alcoholic solution of *o*-phenylene and toluylene diamine, when they separate as yellow needles. The first melts at 217°, the second at 212°. They dissolve with a deep red color in concentrated acids. Their formation may be used to detect and separate the orthophenylene diamines (p. 629).

$\alpha\beta$-**Naphthazine,** $C_{10}H_6(N_2)C_{10}H_6$, *Dinaphthazine*, formerly called naphthase (also thought to be azonaphthalene because it was prepared by heating nitronaphthalene with lime or zinc dust), results upon mixing *o*-naphthylene diamine (1, 2) (p. 626) and β-naphthoquinone (1, 2). It crystallizes and sublimes in yellow needles, that melt at 275°. It dissolves with a violet color in concentrated sulphuric acid; on adding water the solution assumes a yellow color and naphthazine again separates (*Berichte*, 14, 2795).

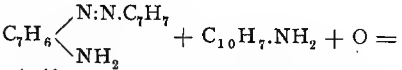
$\beta\beta$-**Naphthazine,** $C_{10}H_6(N_2)C_{10}H_6$, is produced when β-dinaphthylamine is further heated together with benzene diazochloride. It consists of yellow needles that melt at 242° (*Berichte*, 23, 1333).

The phenazines are chromogenic parent substances; they yield dyes by the entrance of salt-forming groups (especially the amido-group). The eurhodines and safranines are included in this series.

1. Eurhodines and Toluylene-Red Group.

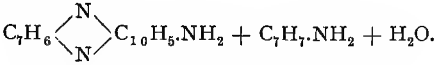
The eurhodine group consists of dyes, which are derived from the phenazines by the introduction of one or more amido-groups (Witt, *Berichte*, 19, 441, 2791; 21, 2418; Kehrmann, 23, 2446; Fischer and Hepp, *Berichte*, 23, 841, 2787). They are formed:—

(1) By the action of orthoamidoazo compounds (p. 643) upon *a*-naphthylamine hydrochloride*:—



$$C_7H_6\left<\begin{matrix}N{:}N.C_7H_7\\NH_2\end{matrix}\right. + C_{10}H_7.NH_2 + O =$$

o-Amido-azo-toluene. *a*-Naphthylamine.

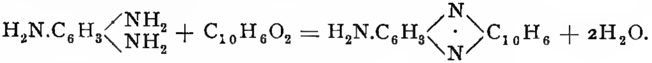


$$C_7H_6\left<\begin{matrix}N\\N\end{matrix}\right>C_{10}H_5.NH_2 + C_7H_7.NH_2 + H_2O.$$

Eurhodine.

The ortho-amido bodies act similarly with the orthophenylene diamines (*Berichte*, 23, 844, 2787).

(2) By the action of ortho-diamines (as unsymmetrical triamidobenzene, p. 625) upon orthodiketones or orthoquinones:—



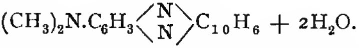
$$H_2N.C_6H_3\left<\begin{matrix}NH_2\\NH_2\end{matrix}\right. + C_{10}H_6O_2 = H_2N.C_6H_3\left<\begin{matrix}N\\N\end{matrix}\right>C_{10}H_6 + 2H_2O.$$

Triamido-benzene. *β*-Naphthoquinone. Eurhodine.

Triamido-benzene reacts in like manner with phenanthraquinone, benzil, isatin, and with the diketones of the paraffin series (*Berichte*, 19, 446). Oxy-orthoquinones and orthodiamines form **oxyeurhodines** (*Berichte*, 23, 2451).

(3) By the action of nitroso-dimethyl aniline upon primary and secondary anilines in which the para-position is occupied (as *β*-naphthylamine and its phenyl derivatives) (*Berichte*, 21, 719):—

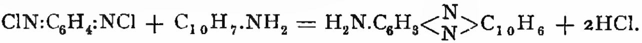
$$(CH_3)_2N.C_6H_4.NO + C_{10}H_7.NH_2 + O =$$



$$(CH_3)_2N.C_6H_3\left<\begin{matrix}N\\N\end{matrix}\right>C_{10}H_6 + 2H_2O.$$

If the *β*-naphthylamine be replaced by its secondary derivatives, the corresponding azonium bases or safranines will be produced.

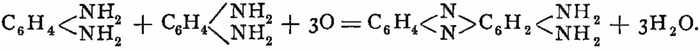
Quinone dichlorimide acts just like nitroso-dimethyl aniline; eurhodines with free amido groups result (*Berichte*, 21, 1599):—



$$ClN{:}C_6H_4{:}NCl + C_{10}H_7.NH_2 = H_2N.C_6H_3<\begin{matrix}N\\N\end{matrix}>C_{10}H_6 + 2HCl.$$

In these methods an indamine always appears at first as a by-product (*Berichte*, 21, 2418).

(4) By the oxidation of ortho-phenylene diamines (2 molecules); here the two nitrogen atoms attack the para-positions, relatively to the two amido-groups, of a second molecule; if amid-groups already occupy the para-position, these will be displaced (Kehrmann, *Berichte*, 22, 1983; Nietzki, *Berichte*, 23, 3039). Thus, ferric chloride converts *o*-phenylenediamine into *diamido phenazine* (O. Fischer, *Berichte*, 22, 355; 23, 841):—



$$C_6H_4<\begin{matrix}NH_2\\NH_2\end{matrix} + C_6H_4\left<\begin{matrix}NH_2\\NH_2\end{matrix}\right. + 3O = C_6H_4<\begin{matrix}N\\N\end{matrix}>C_6H_2<\begin{matrix}NH_2\\NH_2\end{matrix} + 3H_2O.$$

In the same manner *triamidophenazine* is obtained from unsymmetrical triamidobenzene, and *tetramidophenazine* from symmetrical tetramidobenzene (*Berichte*, 22, 3039), etc.

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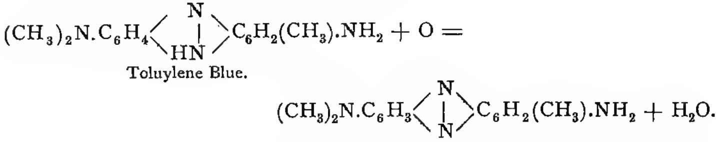
* Indulines result by the use of paramidoazo-compounds (p. 990).

The eurhodines (mono-amido-azines) are feeble bases. Their salts are scarlet red in color; they have not been applied technically. They dissolve in concentrated sulphuric acid with a carmine-red color, which, upon the addition of water passes successively into black, red, and finally red (see safranine). If they be heated to 180° with acids their amido-group is replaced by hydroxyl, with the formation of phenol-like *eurhodols*. Compounds like the last, can be synthetically prepared from oxyorthodiketones by means of orthodiamines (*Berichte*, **23**, 2451).

Amidophenazine, $C_6H_4(N_2)C_6H_3\,NH_2$, has been prepared from *o*-diamido phenazine upon heating it with zinc dust. It consists of red bronze needles, that melt at 265°.

The *toluylene-red* compounds, containing two amido-groups, are more important than the mono-amido-phenazines. They result when diamines are oxidized; more directly by the oxidation of indoamines having free amido groups, even upon boiling the aqueous acid solutions. In this way *toluylene-blue* (from ordinary *m*-toluylene diamine and dimethyl-*p*-phenylene diamine) yields *toluylene-red* (Witt, 1887, *Berichte*, **17**, 931; **19**, 2605; Bernthsen, *Annalen*, **236**, 332):—



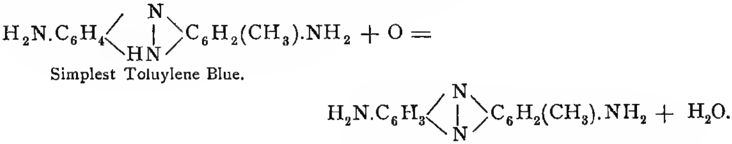
$$(CH_3)_2N.C_6H_4\left\langle\begin{matrix}N\\|\\HN\end{matrix}\right\rangle C_6H_2(CH_3).NH_2 + O =$$

Toluylene Blue.

$$(CH_3)_2N.C_6H_3\left\langle\begin{matrix}N\\|\\N\end{matrix}\right\rangle C_6H_2(CH_3).NH_2 + H_2O.$$

Toluylene Red.

The so called simplest toluylene-blue (from *m*-toluylene diamine and *p*-phenylene diamine) thus gives rise to the *simplest toluylene-red*:—



$$H_2N.C_6H_4\left\langle\begin{matrix}N\\|\\HN\end{matrix}\right\rangle C_6H_2(CH_3).NH_2 + O =$$

Simplest Toluylene Blue.

$$H_2N.C_6H_3\left\langle\begin{matrix}N\\|\\N\end{matrix}\right\rangle C_6H_2(CH_3).NH_2 + H_2O.$$

Simplest Toluylene Red.

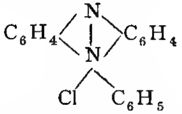
Methyl phenazine results by replacing the two amido groups of the latter compound by hydrogen (this is done through the diazo-derivative); ordinary toluylene red yields dimethylamido-methylphenazine when its NH_2-group is replaced by similar treatment. This is proof that the toluylene-red dyes are phenazine derivatives (Bernthsen).

o-**Diamidophenazine**, $C_6H_4(N_2)C_6H_2(NH_2)_2$ (2, 3), formed by the oxidation of *o*-phenylene diamine with ferric chloride, consists of ruby-red or yellow-brown needles (*Berichte*, **23**, 841). (2, 7)-**Diamidophenazine**, $H_2N.C_6H_3(N_2)C_6H_3.NH_2$, is prepared from dinitro-phenyl-*p*-phenylene diamine, $C_6H_3(NO_2)_2$—$NH.C_6H_4.NH_2$, and consists of dark yellow needles, melting at 280°. **Tetra-amidophenazine**, $(H_2N)_2C_6H_2(N_2)C_6H_2(NH_2)_2$, from tetra-amidobenzene with ferric chloride, consists of brown-colored needles and decomposes about 130°.

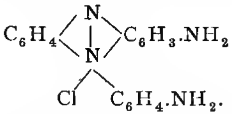
Toluylene Red, $C_{15}H_{16}N_4$, *Dimethyl diamido-toluphenazine* (see above), crystallizes in orange-red needles. It is applied in dyeing under the name *Neutral Red*. Its monacid salts are rose-red in color, the diacid blue, and the triacid green; the last two are only stable in the presence of strong acids. It colors silk and cotton, mordanted with tannin, a scarlet-red.

2. Safranines.

The safranines are probably diamido derivatives of hypothetical *phenyl-phenazonium;* their ammonium salts are dyestuffs (Witt, Nietzki, Bernthsen, *Berichte*, **20**, 19, 179; **19**, 3121, 3163; **21**, 1590):—



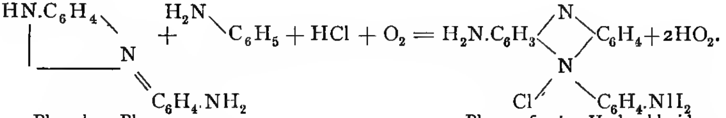
Phenyl-phenazonium Chloride.



Phenosafranine Hydrochloride.

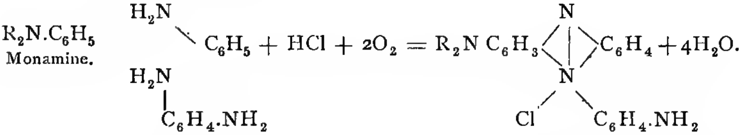
The only known analogue of hypothetical phenyl-phenazonium (without side groups) has been prepared from amidophenyl-α-naphthylamine and phenanthraquinone (*Berichte*, 20, 1183).

The safranines are produced upon oxidizing a mixture of an indoamine and a primary amine (this takes place when their salts are boiled with water). Thus, phenylene blue and aniline yield *phenosafranine:*—



Phenylene Blue. Phenosafranine Hydrochloride.

A simpler procedure consists in applying the components of the indamines, and directly oxidizing the mixture of one molecule of a *p*-phenylene diamine with one molecule of a monoamine and a molecule of a primary amine (by boiling the aqueous solution of their sulphates alone or with chromic acid); an indoamine results at first, and this then combines with the primary amine to produce the safranine (*Berichte*, **21**, Ref. 248):—



Monamine. Diamine. Safranine Hydrochloride.

The formation of the safranine only occurs by this procedure, provided there is a free NH_2-group in the phenylene diamine, if the para-position in the first monamine and the ortho in the second primary amine are unoccupied (*Berichte*, **19**, 3165). Technically the mixture of the diamine and monamine is obtained by the reduction of amido azo-compounds (p. 644).

The safranines are strong bases. They form salts with one, two and three equivalents of the acid; water decomposes the last two series. The monacid salts are reddish-yellow, the diacid blue, and the triacid green in color. The addition of water to the green solution of the safranines in concentrated sulphuric acid causes the same to change to blue, violet and finally red; while the addition of concentrated hydrochloric or sulphuric acid to the reddish-yellow aqueous solution of the primary salts causes the same to pass successively into violet, blue, dark green and eventually light green. The alcoholic solutions usually exhibit a strong yellowish-red fluorescence. The difficult solubility of their nitrates is noteworthy. Reducing agents convert safranines into leuco-compounds, which in the presence of alkalies are rapidly reoxidized by the air to safranines. The free safranine bases or hydroxides are separated from their ammonium salts with difficulty (when warmed with caustic alkalies), and generally show a red color.

The lowest member of the safranines is

Phenosafranine, $C_{18}H_{15}N_4Cl$, formed from *p*-phenylene diamine and aniline. It consists of needles, green in color and having a metallic lustre. It dissolves in water and alcohol with a beautiful red color. Baryta separates the free base, $C_{18}H_{16}N_4O$, from its sulphate; an excess of baryta will substitute two hydroxyls for the two amido groups, producing their *safranol*, $C_{18}H_{10}N_2(OH)_2$ (*Berichte*, **21**, 1591).

Ethyl- and Methyl Safranine, $C_{18}H_{14}(CH_3)N_4Cl$, can exist in two isomeric forms (corresponding to their constitution and different components). *Dimethyl-* and *Diethyl Safranine*, $C_{18}H_{13}(CH_3)_2N_4Cl$. Each of these bodies may occur in three isomeric forms (*Berichte*, **19**, 150, 3164).

Tetra-ethyl Safranine, $C_{18}H_{11}(C_2H_5)_4N_4Cl$. There is but one possible modification of this compound. It is formed from diethyl-*p*-phenylenediamine with diethyl aniline and aniline. It dyes violet and formerly was applied as *amethyst*.

Tolu-Safranine, $C_{18}H_{13}(CH_3)_2N_4Cl$, from toluylene diamine, *o*-toluidine (1 molecule) and aniline (1 molecule), is the chief constituent of common *safranine*, occurring in commerce as a brown paste or yellow-red powder, employed in cotton and silk dyeing, as a substitute for safflor. The necessary base-mixture for its production is obtained from the "aniline oil for safranine." This is partially diazotized and the product broken up into paratoluylene diamine and orthotoluidine by reduction.

The benzidine-tetrazo-dyes have in recent years largely replaced the safranine dye-compounds. A violet dye, **Phenylsafranine**, $C_{20}H_{18}(C_6H_5)N_4Cl$ or $C_{21}H_{20}(C_6H_5)N_4Cl$, is probably identical with **Mauveïne** (Mauvaniline). The latter was the first aniline dye to prove valuable technically (Perkin, 1856), and is obtained by oxidizing aniline oil with potassium bichromate and sulphuric acid. Its sulphate is known in commerce under the name *Rosolan*.

Naphthalene Red, Magdala Red, $C_{30}H_{21}N_4Cl$, is a safranine of naphthalene. It very probably is a diamido-derivative of a naphthyl-naphthazonium salt, $C_{10}H_6(N_2)C_{10}H_6(C_{10}H_7)Cl$ (Julius, *Berichte*, **19**, 1365). It is produced when α-amido-azonaphthalene (p. 914) is heated together with naphthylamine acetate. It is a dark brown powder, that dissolves very readily in alcohol with a bluish-red coloration; the dilute solution exhibits a magnificent cinnabar-red fluorescence. It imparts a beautiful rose red color to silk. Its alcoholic solution is decolorized when boiled with zinc dust, but again assumes a red color on exposure to the air.

The *indulines* and *nigrosines* appear to belong to the safranine class. They are violet-blue to gray-blue dyes. They are formed upon heating various azo- and amido-azobenzenes with aniline hydrochlorides. The simplest induline is *Azophenyl Blue* or *Violaniline*, $C_{10}H_{16}N_3$ (Induline B), which forms upon heating nitrobenzene, aniline, hydrochloric acid and iron filings (Coupier's method), or amido-azobenzene with aniline hydrochloride (Caro):—

$$C_6H_6.N_2.C_6H_4.NH_2 + C_6H_5.NH_2.HCl = C_{18}H_{15}N_3 + NH_4Cl.$$

Here, as in analogous reactions, the first product is *azophenine*, $C_{30}H_{24}N_4$, which represents a dianilido quinone-dianilide (p. 700). The *indulines* result by the continued action of the azophenine upon anilines. They are also prepared by heating together nitroso-diphenylamine and the amine hydrochlorides. Hence, the indulines are anilido-anilide derivatives of the phenazines (Witt, *Berichte*, 20, 2659; O. Fischer and Hepp, *Berichte*, 20, 2479; 21, 2617). The induline salts are usually insoluble in water. The easily soluble sulpho- acids have been used in silk dyeing as substitutes for indigo.

The *rosindulines* are peculiar red dyes formed upon heating nitrosophenyl- or nitrosoethyl-α-naphthylamine, $C_{10}H_7.N(NO).C_6H_5$, with the HCl-anilines, and by heating benzene azo-α-naphthylamines with anilines (*Berichte*, 21, 2631; 23, Ref. 391).

Fluorindenes, closely allied to the indulines and azophenine, are produced by the protracted heating of azophenine or amidophenazines alone or with ortho-diamines. They dissolve in alcohol with beautiful fluorescence and form greenish-blue colored fluorescent salts (*Berichte*, 23, 2789).

Aniline Black, $C_{18}H_{15}N_3$ or $C_{30}H_{27}N_5$(?), most probably belongs to the indulines, and is formed in the oxidation of aniline by means of potassium chlorate in the presence of copper or vanadium salts. It is a dark-green amorphous powder, insoluble in the ordinary reagents. It is used in calico printing as a black color, its formation being first effected upon the fibre of the material.

Naturally occurring compounds, the constitution and synthesis of which have not been definitely established, will be discussed in special groups in the remaining pages.

ALKALOIDS.

By this term we know all nitrogenous vegetable compounds of basic character, or their derivatives, from which bases may be isolated. Many of them (betaïne, asparagine, theïne), have, in accord with their constitution, been already discussed with the various amido-derivatives; the most of those remaining which have been studied recently, show themselves to be derivatives of the pyridine and quinoline bases. Several have been prepared artificially (piperidine, conine). Only the most important members of this insufficiently investigated class will be mentioned here. Like the benzene derivatives they have much in common in their whole deportment. They are the chief constituents of the active principles of the vegetable drugs employed as medicines or poisons.

Some alkaloids contain no oxygen, and then are generally liquid and volatile. Most of them do, however, contain that element, and are solid and non-volatile. Nearly all are tertiary amines; some, however (like the hydrides of the pyridine nucleus, p. 936), belong to the secondary amines. Tannic acid, phospho-molybdic acid, platinic chloride, and many double salts (like HgI.2KI) precipitate all these bases from their aqueous solutions. The bases are regained from these compounds by alkalies.

Sparteïne, $C_{15}H_{26}N_2$, is a volatile alkaloid which does not contain oxygen. It occurs in *Spartium scoparium*, and is a colorless, thick oil, boiling at 311°. It has a strong alkaline reaction, is narcotic and is also a diacid base. A methyl group is eliminated when it is heated with hydrochloric or hydriodic acid. It forms *γ*-methyl pyridine when distilled with lime (*Berichte*, 21, 825). Hence, sparteïne is closely allied to dipicolyl methane, $CH_2(CH.C_5H_4N)_2$ (from methylal and picoline) (*Berichte*, 21, 3103).

Opium Bases.

In opium, the dried juice of the green seed capsules of poppy (Papaver somniferum) we find not only meconic acid and meconine (p. 794) but a series of bases, of which may be mentioned :—

Morphine,	$C_{17}H_{19}NO_3$	Papaverine,	$C_{20}H_{21}NO_4$
Codeïne,	$C_{18}H_{21}NO_3$	Narcotine,	$C_{22}H_{23}NO_7$
Thebaïne,	$C_{19}H_{21}NO_3$	Narceïne,	$C_{23}H_{29}NO_9$.

Morphine, $C_{17}H_{19}NO_3 + H_2O$, crystallizes from alcohol in prisms, tastes bitter, and in small quantities produces sleep. It shows an alkaline reaction, and represents a tertiary, monacid base. Its officinal hydrochloride, $C_{17}H_{19}NO_3HCl + 4H_2O$, forms delicate, silky needles.

The solutions of morphine and its salts are colored dark blue by ferric chloride; the solution in concentrated sulphuric acid acquires a blood-red coloration on the addition of a little nitric acid. It contains two hydroxyl groups, $C_{17}H_{17}(OH)_2NO$, deports itself as a dihydric phenol, dissolves in potassium hydroxide, and yields alkyl and acid derivatives. It forms quinoline, phenanthrene (with phenanthrene-quinoline) pyridine and pyrrol, on distillation with zinc dust. When methylated to its fullest extent, morphine undergoes a rearrangement similar to that of piperidine and conine (p. 950). The hydroxide obtained from ethyl morphine by addition of methyl iodide and the action of silver oxide, passes into the phenanthrene derivative (*Annalen*, 222, 235) on the application of heat. The nitrogen atom splits off in the form of dimethylamine or oxyethyl dimethylamine $(CH_3)_2N.CH_2.CH_2(OH)$. The latter is related to morpholine (pp. 957, 981), hence morphine appears to represent a phenanthrene-morpholine derivative (Knorr, *Berichte*, 22, 1113; 22, Ref. 758).

Codeïne, $C_{18}H_{21}NO_3$, **Methyl Morphine**, $C_{17}H_{17}\begin{pmatrix}OH\\O.CH_3\end{pmatrix}NO$, is contained in opium, and is obtained from morphine by means of methyl iodide and potassium hydroxide. From ether it crystallizes in large prisms, melting at 150° (*Berichte*, 19, 794).

Thebaïne, $C_{19}H_{23}NO_3 = C_{17}H_{17}(O\,CH_3)_2NO$, consists of silvery plates, melting at 193°. It breaks down into $2CH_3Cl$ and *morphothebaïne*, when heated with concentrated hydrochloric acid. This new isomeric base melts at 180°.

Silver oxide converts its methyl iodide derivative into an ammonium hydroxide, which breaks down quite readily on the application of heat (*Berichte*, 19, 794).

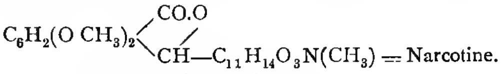
Papaverine, $C_{20}H_{21}NO_4$ (*Berichte*, 18, Ref. 636), consists of colorless prisms melting at 148°. It very probably is a tetramethoxyl derivative of benzylisoquinoline (Goldschmidt, *Berichte*, 20, 623; 21, Ref. 653; Roser, *Annalen*, 254, 357):—

$$C_6H_3(O.CH_3)_2.CH_2.C_9H_4(O.CH_3)_2N = \text{Papaverine.}$$

Hot hydriodic acid decomposes it into $4CH_3I$ and the base *papaveroline*, $C_{16}H_9(OH)_4N$. Potassium permanganate oxidizes it to *papaveraldine*, $C_{20}H_{19}NO_5$, which in all probability is a ketone, $C_6H_3(O.CH_3)_2.CO.C_9H_4(O.CH_3)_2N$.

Further oxidation gives rise to two decompositions, (1) that of the benzene nucleus whereby dimethoxy-cinchoninic acid, $C_9H_4(O.CH_3)_2N.CO_2H$ and $\alpha\beta\gamma$-pyridine tricarboxylic acid are produced; (2) that of the isoquinoline nucleus, resulting in formation of veratric acid and metahemipinic acid (p. 794) (*Berichte*, 21, Ref. 787). Papaverine breaks down into veratric acid and dimethyl isoquinoline when fused with caustic potash. Consult *Berichte*, 22, 102, 755, for papaverine ammonium bases.

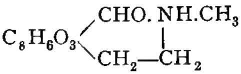
Narcotine, $C_{22}H_{23}NO_7$, is separated from morphine by potassium hydroxide, in which it is insoluble. It crystallizes from alcohol in shining prisms, and melts at 176°. In constitution it is intimately related to papaverine. It contains not only the benzene, but also the isoquinoline nucleus. It very likely represents a *meconine-hydrocotarnine* (Roser, *Berichte*, 23, Ref. 16, 19; *Annalen*, 254, 357):—



$$C_6H_2(O\,CH_3)_2\left\langle\begin{array}{l} CO.O \\ \quad / \\ CH—C_{11}H_{14}O_3N(CH_3) \end{array}\right. = \text{Narcotine.}$$

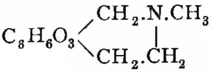
Meconine-hydrocotarnine.

When boiled with water narcotine is decomposed into meconine, $C_{10}H_{10}O_4$ (p. 794), and **cotarnine**, $C_{12}H_{13}NO_3.H_2O$. The latter appears to be an aldehyde with an open pyridine chain, which in the cotarnine salts and hydro-cotarnine is closed up as a pyridine ring (and isoquinoline ring) (*Berichte*, 22, Ref. 27):—



$$C_8H_6O_3\left\langle\begin{array}{l} CHO.\ NH.CH_3 \\ \qquad\quad | \\ CH_2—CH_2 \end{array}\right.$$

Cotarnine.



$$C_8H_6O_3\left\langle\begin{array}{l} CH_2.N.CH_3 \\ \qquad\ | \\ CH_2.CH_2 \end{array}\right.$$

Hydrocotarnine.

Potassium permanganate oxidizes cotarnine or cotarnone to *cotarnic acid*, $C_6H\left(\begin{smallmatrix}O\\O\end{smallmatrix}>CH_2\right)\left\langle\begin{smallmatrix}O\,CH_3\\(CO_2H)_2\end{smallmatrix}\right.$, which can be further changed to *methyl methylene gallic acid*, $C_6H_2\left(\begin{smallmatrix}O\\O\end{smallmatrix}>CH_2\right)\left\langle\begin{smallmatrix}O.CH_3\\CO_2H\end{smallmatrix}\right.$, and gallic acid, $C_6H_2(OH)_3.CO_2H$.

Narceïne, $C_{23}H_{29}NO_9$ (see above), appears to be a naphthalene derivative (*Berichte*, 21, Ref. 249).

A compound allied to papaverine and narcotine is

Hydrastine, $C_{21}H_{21}NO_6$, which occurs together with *berberine*, $C_{20}H_{17}NO_4 + 4\frac{1}{2}H_2O$, in the roots of *Hydrastis canadensis* (*Berichte*, 23, 404, 2897).

Cinchona Bases.

The *cinchona barks* contain, in addition to tannin and quinic acid (p. 785), a series of bases, the most important of which are:

Quinine, $C_{20}H_{24}N_2O_2$,
Cinchonine, $C_{19}H_{22}N_2O$,
Conquinine, $C_{20}H_{24}N_2O_2$,
Cinchonidine, $C_{19}H_{22}N_2O$.*

Quinine and cinchonine are present in large quantity in so-called *Calisaya* bark, while the bases conquinine or quinidine and cinchonidine, isomeric with them, predominate in other varieties of quinia barks.

Quinine, $C_{20}H_{24}N_2O_2$, is found as high as 2–3 per cent. in the yellow Calisaya bark. It crystallizes with $3H_2O$ in prisms, or when anhydrous (from alcohol and ether) in silky needles, melting at 177°. It reacts alkaline, tastes bitter, and being a diacid base forms primary and secondary salts.

The neutral *sulphate*, $(C_{20}H_{24}N_2O_2)_2H_2SO_4 + 8H_2O$, and the primary *hydrochloride*, $C_{20}H_{24}N_2O_2.HCl + 2H_2O$, are employed in medicine. The former consists of long, shining needles, which fall to a white powder on exposure. It dissolves readily in dilute sulphuric acid, the solution exhibiting a beautiful blue fluorescence.

When chlorine water and then ammonia are added to the solution of a quinine salt, there is produced a green precipitate, dissolving in an excess of ammonium hydroxide with an emerald-green color. On adding an alcoholic iodine solution to the sulphate in acetic acid, a *periodide*, called *herapathite*, is precipitated. This crystallizes in emerald-green plates with golden lustre, and polarizes light the same as tourmaline.

Quinine is a tertiary diamine, and with ~~metallic~~ iodide yields the iodides, $C_{20}H_{24}N_2O_2.CH_3I$ and $C_{20}H_{24}N_2O_2.2CH_3I$. The first of these yields the so-called methyl quinine, $C_{20}H_{23}(CH_3)N_2O_2$, when it is boiled with caustic potash.

Cinchonine, $C_{19}H_{22}N_2O$, occurs principally in the gray quinia bark (China Huanaco) (upwards of 2.5 per cent.) It crystallizes from alcohol in white prisms, sublimes in needles in a current of hydrogen, and melts about 250°. Like quinine it seems to dissipate fever, but to a less degree.

Quinine and cinchonine contain one hydroxyl, and the former an additional methoxyl group:

$C_{19}H_{21}(OH)N_2$
Cinchonine.

$C_{19}H_{20}(O.CH_3)(OH)N_2$.
Quinine.

They yield acetyl derivatives when heated with acetic anhydride. Quinine

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* The quinoïdine of commerce generally consists of cinchonidine and sometimes of conquinine.

heated to 150° with hydrochloric acid splits off the methyl group, with formation of apoquinine, $C_{19}H_{20}(OH)_2N_2$, which deports itself like a bivalent phenol. Phosphorus pentachloride converts cinchonine (by replacing its hydroxyl group) into cinchonine chloride, $C_{19}H_{21}ClN_2$, quinine into quinine chloride, $C_{20}H_{23}ClN_2O$, and these compounds boiled with alcoholic potash yield *cinchene* and *quinene* :—

$$\underset{\text{Cinchene.}}{C_{19}H_{20}N_2} \quad \text{and} \quad \underset{\text{Quinene.}}{C_{20}H_{22}N_2O},$$

which, when heated to 190° together with concentrated hydrochloric or hydrobromic acid, give up ammonia and absorb water, thus forming *apocinchene* and *apoquinene* :—

$$\underset{\text{Apocinchene.}}{C_{19}H_{19}NO} \qquad \underset{\text{Apoquinene.}}{C_{20}H_{21}NO_2}.$$

Apocinchene manifests a phenol character, and may be considered a γ-phenolquinoline, $C_9H_6N.C_6H_4.OH$ (p. 971), in the benzene nucleus of which alkyls are yet present, $C_9H_6N.C_6H_2(C_4H_{10})OH$ or $C_9H_6N.C_{10}H_{12}.OH$. It is not known in what manner the second N-atom in cinchonine is combined with the side-chain (Koenigs, *Berichte*, 20, 2688, 2526, 2669) (see also Skraup, *Berichte*, 22, Ref. 332, 578).

Oxidation converts cinchonine into cinchoninic acid (γ-quinoline carboxylic acid, p. 972), whereas quinine yields quininic acid, (methoxy γ-quinoline carboxylic acid, $C_9H_5(O.CH_3)N.CO_2H$, p. 973). More energetic oxidation, with potassium permanganate, changes cinchonine and quinine into αβγ-pyridine tricarboxylic acid and cinchomeronic acid (p. 948). If cinchonine be fused with alkalies it forms quinoline, C_9H_7N (together with β-ethyl pyridine and fatty acids), but from quinine under like treatment we get a methyloxyquinoline, $C_9H_6(O.CH_3)N$ (p. 969).

Bases from Strychnos.

In the fruit of the different strychnos, principally in that of Strychnos nux vomica and in St. Ignatius' bean (Strychnos Ignatii), are found two very poisonous bases: Strychnine and brucine.

Strychnine, $C_{21}H_{22}N_2O_2$, crystallizes in four-sided prisms, melting at 284°, reacting alkaline and possessing an extremely bitter taste. It is a tertiary amine, and when fused with potassium hydroxide yields quinoline and indol. Consult *Berichte*, 23, 2721, upon the methyl strychnines.

Brucine, $C_{23}H_{26}N_2O_4$, crystallizes, containing four molecules of water, in prisms, and melts at 178° when anhydrous. It dissolves with a red color in concentrated nitric acid. On application of heat it becomes yellow and violet after the addition of stannous chloride. When distilled with potassium hydroxide it yields β-ethyl pyridine and two collidines.

Strychnine and brucine probably contain a quinoline nucleus; in strychnine there is also present a phenylpyridine, and in brucine a dioxymethyl phenylpyridine (*Berichte*, 21, 451, 813).

Solanum Bases.

In some varieties of Solanum there are found three isomeric alkaloids of very similar constitution, $C_{17}H_{23}NO_3$. They are *atropine*, *hyoscyamine* and *hyoscine*. If they are introduced in very small quantity into the eye they cause dilatation of the pupil and are therefore employed in the treatment of the eyes. All three decompose into tropic acid (and atropic acid, p. 813), and a base, $C_8H_{15}NO$, when heated with hydrochloric acid or baryta water:—

$$C_{17}H_{23}NO_3 + H_2O = C_8H_{15}NO + C_9H_{10}O_3;$$

by this reaction *tropine* is formed from atropine and hyoscyamine, but from hyoscine we get isomeric *pseudotropine*. By the same treatment dextro-tropic acid yields dextro-atropine and lævo-tropic acid lævo-atropine (*Berichte*, **22**, 2591). Conversely, inactive atropine is again recovered by evaporating tropic acid and atropine with dilute hydrochloric acid.

Atropine, daturine, $C_{17}H_{23}NO_3$, is prepared from the deadly nightshade (Atropa belladonna) and *Datura strammonium* by a rearrangement of the hyoscyamine present in them (*Berichte*, 21, 1719). It crystallizes from alcohol in small prisms, melting at 114°. It is optically inactive. *Dextro-atropine*, from dextro-tropic acid, forms white shining needles, melting at 110-111°; *lævo-atropine* is a crystalline powder, that melts at 111°. It is similar to hyoscyamine, but not identical with it. The supposed rearrangement of atropine into hyoscyamine (*Berichte*, 21, 1717, 2777) is due, according to Ladenburg, to the presence of considerable hyoscyamine in the atropine (*Berichte*, 21, 3069).

Hyoscyamine, $C_{17}H_{23}NO_3$, occurs in the seeds of *Hyoscyamus niger*, in *Atropa belladonna* and in *Datura strammonium*. It crystallizes from chloroform in shining needles, and melts at 108.5°. **Hyoscine**, $C_{17}H_{23}NO_3$, is a viscous liquid found in henbane.

Duboisine, from *Duboisia myoporoides*, is either hyoscyamine or hyoscine (*Berichte*, 20, 1661).

Belladonine, $C_{17}H_{23}NO_3$, resembles these alkaloids. It occurs with atropine, and is likewise decomposed into tropic acid and oxy-tropine, $C_8H_{15}NO_2$ (*Berichte*, 17, 152, 383).

Just as tropine yields atropine with atropic acid, so it is capable of entering combination with other acids producing ester-like derivatives, which have been called *tropeïnes* (Ladenburg, *Annalen*, **217**, 82). Of these phenylglycolyl-tropeïne or **Homatropine**, $C_5H_7N(CH_3).C_2H_4.O.CO.CH(OH).C_6H_5$, is noteworthy. It is obtained from tropine and mandelic acid. It is employed as a substitute for atropine, and is applied in the form of hydrobromide.

Cocaïne, $C_{17}H_{21}NO_4$, is present in the leaves of Erythroxylon coca. It crystallizes in colorless prisms, melting at 98°. It is a very superior local anæsthetic and is applied in the form of hydrochloride. When it is digested with hydrochloric acid it breaks down into ecgonine, $C_9H_{15}NO_3$, benzoic acid and methyl alcohol:—

$$C_{17}H_{21}NO_4 + 2H_2O = C_9H_{15}NO_3 + C_7H_6O_2 + CH_3.OH.$$

It yields benzoyl ecgonine, $C_9H_{14}(C_7H_5O)NO_3$, when boiled with water. Cocaïne is, therefore, a methylated benzoylecgonine (see below).

Conversely, cocaïne can be again re-formed from ecgonine by heating it together with benzoic anhydride and methyl iodide, or from benzoyl ecgonine with methyl iodide and sodium ethylate (Merck, *Berichte*, 18, 2953). It is more readily obtained by the etherification of benzoyl ecgonine with methyl alcohol and hydrochloric acid (Einhorn, *Berichte*, 21, 47), or by introducing benzoyl into ecgonine ester (*Berichte*, 21, 3202, 3336). This procedure is used at present in its preparation on a large scale.

Crude cocaïne, obtained by extracting coca-leaves, contains a series of amorphous alkaloids (cocamine, hygrine, *Berichte*, 21, 665, 675), from which it is separated with great difficulty. These associated alkaloids are also derivatives of ecgonine, and contain isatropic acid (isatropyl cocaïne), truxillic acid and isocinnamic acid (p. 812) instead of benzoic acid. All eliminate ecgonine when digested with hydrochloric acid (Liebermann, *Berichte*, 21, 3196), and from this the pure cocaïne is prepared synthetically.

Ordinary cocaïne is lævo-rotatory. **Dextro-Cocaïne** (*Berichte*, 23, 508, 926) occurs with it in slight amount. The latter is obtained pure from dextro-ecgonine (*Berichte*, 23, 468, 982). It forms prismatic crystals, melting at 43–45°.

Ecgonine, $C_9H_{15}NO_3 + H_2O$, produced in the decomposition of cocaïne, is very soluble in water, more sparingly in alcohol, and consists of prismatic crystals that melt at 205° (at 140° when dry). Its esters are formed when hydrochloric acid gas is conducted into its alcoholic solution (*Berichte*, 21, 3336). Benzoic anhydride acting on aqueous ecgonine (*Berichte*, 21, 3198, 3372) produces **Benzoyl Ecgonine,** $C_9H_{14}(C_7H_5O)NO_3 + 4H_2O$.

In the anhydrous state this melts at 195°. Ecgonine is lævo-rotatory. It passes into the dextro variety when digested with caustic potash. The latter melts at 254° (*Berichte*, 23, 470, 979), and yields dextro-cocaïne.

The withdrawal of water from ecgonine (by boiling with $POCl_3$) produces *anhydroecgonine*, $C_9H_{13}NO_2$, melting at 235° (*Berichte*, 20, 1221). This is an unsaturated acid, which potassium permanganate converts into the oxyacid, ecgonine. α-Ethyl pyridine results upon distilling ecgonine with lime or zinc dust (*Berichte*, 22, 1126, 1362). The preceding compounds, therefore, are derivatives of *n*-methyl tetrahydropyridine, in which one of the side groups is in the α-position (Einhorn, *Berichte*, 20, 1228). *Ecgonine* is *n-methyl-tetrahydropyridine–β–oxy-propionic acid*:—

$$C_5H_4(H_3)N(CH_3).CH(OH).CH_2.CO_2H = \text{Ecgonine};$$

anhydroecgonine is the corresponding acrylic acid:—

$$C_5H_4(H_3)N(CH_3).CH : CH.CO_2H = \text{Anhydroecgonine},$$

and cocaïne is the benzoyl-ecgonine-methyl ester:—

$$C_5H_4(H_3)NCH_3.CH(O.C_7H_5O).CH_2.CO_2.CH_3 = \text{Cocaïne}.$$

Anhydroecgonine is the tetrahydro-*n*-methyl derivative of the pyridylacrylic acid (p. 947), ecgonine, the derivative of pyridyl-β-lactic acid (*Berichte*, 23, 224). Tropidine is obtained from anhydroecgonine by heating the latter with hydrochloric acid to 280°, when it loses carbon dioxide (*Berichte*, 23, 1338). Potassium permanganate oxidizes ecgonine to tropic acid, $C_8H_{13}NO_4$ (*Berichte*, 23, 2518, 2889).

There remain other alkaloids which have been poorly investigated: mention may be made of the following:—

Veratrine, $C_{32}H_{49}NO_9$, **Cevadine.** This occurs, together with veratric acid (p. 779), and other alkaloids, in the white hellebore (from V. album) and in the Sabadilla seeds (from V. Sabadilla). It crystallizes from alcohol in prisms, and melts at 205°. It dissolves in sulphuric acid with a yellow color, which gradually changes to blood-red. It yields β-picoline (*Berichte*, 23, 2707) by dry distillation.

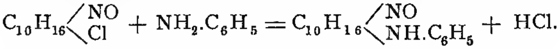
Sinapine, $C_{16}H_{23}NO_5$, occurs as sulphocyanate in white mustard. Free sinapine is very soluble, and decomposable. When boiled with alkalies it decomposes into choline and *sinapic acid*, $C_{11}H_{12}O_5$, which is a butylene gallic acid.

TERPENES.

The terpenes are hydrocarbons, analogous to turpentine oil. They have the formula $C_{10}H_{16}$ or $(C_5H_8)_n$, and are contained in the *volatile* or *ethereal* oils obtained in the distillation of various plants (chiefly Coniferæ and Citrus species). The terpenes that have been thus isolated are very numerous; their properties vary but little, and they have heretofore been considered either as chemical or physical isomerides, according to their origin. In recent years investigators have succeeded in reducing them to a few (8–10) pure parent-substances, and referring them to individual groups. Their distinction and classification depends upon the power that some possess, of combining with one or two molecules of bromine or a halogen hydride, or with nitrosyl chloride (with two or four affinities), whereas others are incapable of forming addition products (see Wallach, *Annalen*, 230, 225; 239, 1; 245, 241; 252, 106, etc.).

The addition of the halogens or halogen hydrides succeeds best in a glacial acetic acid solution at low temperatures. The additive products revert to the terpenes when heated with sodium acetate (in glacial acetic acid solution).

The *nitroso-chlorides* of the terpenes, $C_{10}H_{16}\begin{matrix}\diagup Cl\\ \diagdown NO\end{matrix}$ (p. 112), were first obtained by the action of nitrosyl chloride, NOCl, upon the pinenes and limonenes (Tilden). A simpler method for their preparation consists in shaking a chilled mixture of terpene and amyl nitrite (or ethyl nitrite) with concentrated hydrochloric acid, and then adding alcohol or glacial acetic acid (Wallach, *Berichte*, 21, Ref. 622; 22, Ref. 583). The nitroso-chlorides are crystalline compounds, which melt above 100°. They form *nitrolamines* with organic bases (amines, anilines, piperidines) (they thus resemble the nitrosates of the alkylenes, (p. 112) (*Berichte*, 21, Ref. 584):—



$$C_{10}H_{16}\begin{matrix}\diagup NO\\ \diagdown Cl\end{matrix} + NH_2.C_6H_5 = C_{10}H_{16}\begin{matrix}\diagup NO\\ \diagdown NH.C_6H_5\end{matrix} + HCl.$$

The elimination of hydrogen chloride in this reaction, which occurs with some bases, leads to the formation of *Nitroso-terpenes*, $C_{10}H_{15}(NO)$.

Several terpenes (as the dipentenes) unite with N_2O_4 and form *nitrosates* C_6

$H_4(NO).O.NO_2$ (p. 112). Terpinene and phillandrene yield *nitrosites*, $C_6H_4(NO)(O.NO_2)$ with N_2O_3.

The terpenes are closely related, so far as constitution is concerned, to ordinary *cymene*, $C_{10}H_{14}$ (*p*-methylpropyl benzene, $C_3H_7.C_6H_4.CH_3$); they can be readily converted into it by the withdrawal of two hydrogen atoms (see below and p. 577). This occurs by their oxidation to *p*-toluic and terephthalic acids, $C_6H_4(CO_2H)_2$. Therefore, the terpenes may be viewed as benzene additive products—as dihydrocymenes, $C_{10}H_{14}(H_2)$.

In accordance with the generally accepted structure of the benzene nucleus several *p*-dihydrocymenes are possible; they contain in addition two divalent ethylene unions, and therefore can form additive products with four affinities (p. 567) (Compare citrene). Again, there are other terpenes which contain but *two* free affinities, or are not capable of forming additive products (pinene, camphene, etc.). These very probably originate from differently constituted benzene nuclei with diagonal or para-linkages (p. 564). This seems evident from their lower refractive power (Brühl, *Berichte*, **21**, 145, 467). Wallach considers that the conclusions drawn from the molecular refractions are unreliable (*Berichte*, **21**, Ref. 342; **22**, Ref. 584).

(1) PINENE AND CAMPHENE GROUP.

These combine with but one molecule of the halogen hydrides. The first forms a compound with nitroso-chloride, the second does not.

(1) *Pinene* — $C_{10}H_{16}$ — is the chief ingredient of the turpentine oil prepared from the different varieties of pine, of eucalyptus oil, juniper-berry oil, sage oil, etc.

The resinous juice, called turpentine, exuding from various coniferæ, consists of a solution of resin in turpentine oil, which distils with steam while the resin (colophony) remains behind.

Oil of turpentine is a colorless peculiar-smelling liquid, boiling from 158–160°; its sp. gr. equals 0.856–0.87. It is almost insoluble in water, is miscible with absolute alcohol and ether, dissolves sulphur, phosphorus, resins, caoutchouc, and, therefore, serves for the preparation of oil colors and varnishes.

The turpentines, according to their origin, show some differences, especially in their optical rotatory power.

The German turpentine oil (from *Pinus silvestris* and Abies excelsa), the French (from *Pinus maritima*), called *Terebenthene*, the Venetian (from *Larix europæa*), are lævo-rotatory, while the English (from *Pinus australis*) called *Australene*, is dextro-rotatory. This is also true of the terpene from oil of wormwood, and from the oil of mint.

The basis of these various turpentine oils seems to be a *Dextro-pinene* and a *lævo-pinene* (as in the case of the tartaric acids). The Russian and Swedish turpentine oils consist mainly of cinene and sylvestrene (see below).

Oil of turpentine slowly acquires oxygen from the air (with ozone formation) and resinifies with production of acids (formic, acetic); at the same time small quantities of cymene are formed. When turpentine is boiled with nitric acid, different fatty acids, terebinic acid, pyrocinchonic acid, toluic acid and terephthalic acid result. Chromic acid converts it into terebinic acid and terpenylic acid (p. 470).

Turpentine oil (pinene) heated to 250–300° is converted into dipentene, $C_{10}H_{16}$ (see below) and meta-terebenthene, $C_{20}H_{32}$ (boiling at 260°). Turpentine oil heated together with iodine in a vessel in connection with a return cooler undergoes a violent reaction and forms cymene, $C_{10}H_{14}$. The same compound is produced on heating the dichloride, $C_{10}H_{16}Cl_2$, when it loses two molecules of hydrogen chloride. **Terpene Tetrahydride**, $C_{10}H_{20}$, is produced when turpentine oil is heated with hydriodic acid or phosphonium iodide. It boils at 170–172°. **Menthene** is a dihydride, $C_{11}H_{18}$ (p. 1007).

Pinene unites with a molecule of chlorine and bromine, forming liquid compounds that are not very characteristic. In the same manner it combines with but one molecule of hydrochloric or hydrobromic acid—the products being solids, which cannot absorb additional halogens or halogen hydrides. It is therefore very probable that pinene contains but one divalent union (see above).

Pinene Dichloride, $C_{10}H_{16}Cl_2$, and **Pinene Dibromide**, $C_{10}H_{16}Br_2$, are unstable liquids. When heated they break down into halogen hydrides and cymene.

Pinene Hydrochloride, $C_{10}H_{16}.HCl$, is produced on conducting HCl gas into well-cooled pinene. The hydrochloride (called *artificial camphor*) yields crystals resembling those of camphor, has the odor of the latter, melts at 125°, and boils at 208°. The hydrochloride of lævo-pinene is lævo-rotatory, while that from dextro-pinene is dextro-rotatory. **Pinene Hydrobromide**, $C_{10}H_{17}Br$, formed like the hydrochloride, melts at 90° and has a higher boiling point than the chloride.

Solid camphene (see below) results when the preceding compounds lose hydrogen chloride or bromide. This occurs when they are boiled with glacial acetic acid and sodium acetate.

Pinene Nitroso-chloride, $C_{10}H_{16}(NO)Cl$, obtained by means of nitrosylchloride, or amyl nitrite, glacial acetic acid and hydrochloric acid, melts at 103°; the **bromide**, $C_{10}H_{16}(NO)Br$, at 92°. Piperidine and the chloride yield *Nitrolamine*, $C_{10}H_{18}(NO).NC_5H_{10}$, but with other bases the product is *Nitrosoterpene*, $C_{10}H_{15}(NO)$, melting at 132°.

By the prolonged action of moist hydrogen chloride upon pinene, the latter rearranges itself to dipentene, a *dihydrochloride*, $C_{10}H_{18}Cl_2$, that melts at 50°, and is identical with dipentene-dihydrochloride (see below).

If turpentine oil containing water be permitted to stand for some time with nitric acid and alcohol (*Annalen*, 230, 248), or dipentene dihydrochloride, $C_{10}H_{18}Cl_2$, (p. 1002), with aqueous alcohol, so called *Terpine Hydrate*, $C_{10}H_{20}O_2 + H_2O$, will result. This is readily soluble in hot water, alcohol and ether. It is odorless, and forms large rhombic crystals, that melt at 117° in a capillary tube. Above 100° it loses water and changes to *terpine*, $C_{10}H_{20}O_2 = C_{10}H_{18}(OH)_2$, subliming in needles, that melt at 104° and distil at 258°. Terpine reacts like a glycol. When digested with nitric acid it forms a dinitric ester.

Dihydrohaloid compounds, $C_{10}H_{18}X_2$, of dipentene, are formed when terpine, or terpine hydrate, is shaken with the haloid acids. Boiling sulphuric acid (1 part : $2H_2O$) causes terpine hydrate to lose water and form *Terpineol*, $C_{10}H_{17}(OH)$ (p. 1007). Bromine converts it into dipentene tetrabromide, $C_{10}H_{16}Br_4$ (melting at 125°) (*Annalen*, 230, 253; 239, 8).

Terpine hydrate and terpineol lose additional water by continued heating with sulphuric acid and yield dipentenes, terpinenes and terpinolenes (see below). Terpineol at the same time, yields isomeric cineol (*Annalen*, 246, 236).

(2) **Camphene,** $C_{10}H_{16}$, is the solid terpene, obtained from pinene halogen hydride, by the elimination of the haloid acid. A better method to pursue in its preparation is to boil bornyl chloride, $C_{10}H_{17}Cl$, with aniline.

The camphenes from different sources differ from each other in rotatory power: *Terecamphene*, from terebenthene, is lævo-rotatory, austracamphene, from Australene, is dextro-rotatory, while *Borneo-camphene* (Borneen), from borneol chloride, is inactive. They are crystalline masses, melting at 49°, and boiling at 156–157°. Chromic acid oxidizes them to ordinary camphor (active and inactive).

Camphene and hydrochloric acid form a liquid, unstable additive product, $C_{10}H_{16}.HCl$, which is readily resolved into its components. Bromine does not produce an additive, but rather a substitution product, $C_{10}H_{15}Br$. Nor is it able to form a nitroso-chloride. The assumption therefore that there are no divalent unions in camphene, but two para-unions of the benzene nucleus is, in the opinion of Wallach, unestablished (*Berichte*, 22, Ref. 585).

2. LIMONENE AND DIPENTENE GROUP.

These combine with two molecules of bromine or of a halogen hydride, but not with N_2O_3.

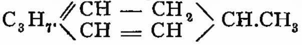
1. **Dextro-limonene,** $C_{10}H_{16}$, *Citrene*, hesperidene, carvene, is the oil of *Citrus aurantiæ*, and the chief ingredient of cedar oil, cumin oil and dill oil. It occurs associated with pinene in lemon oil. *Lævo-limonene* occurs together with lævo-pinene (boiling at 160°) in pine oil (from *Pinus sylvestris*), and may be isolated from it by fractional distillation (*Berichte*, 21, Ref. 624.)

Both limonenes are agreeably smelling liquids, sp-gr. 0.846 at 20°, and boil at 175–176°. They differ from each other, even in their derivatives, almost exclusively in their opposite rotatory power.

Bromine converts each into a characteristic **Tetrabromide,** $C_{10}H_{16}Br_4$, that crystallizes in large prisms, melting at 103°. The one is dextro- and the other lævo-rotatory. They combine with two molecules of the halogen hydrides to compounds of the type $C_{10}H_{18}X_2$; these are identical with the dipentene derivatives; there has therefore been a rearrangement of the limonenes into dipentenes.

The **Dextro-Nitroso-chloride,** $C_{10}H_{16}(NO)Cl$, and the *lævo-nitroso-chloride* result by the action of amyl nitrite and hydrochloric acid upon dextro and lævo-limonene. Both melt at 103°. They differ from each other solely in rotatory power. Boiling alcohol converts the lævo-nitroso-chloride into **Dextro-nitroso-limonene**, $C_{10}H_{15}(NO)$ (by elimination of HCl), which melts at 72° and is identical with **dextro-carvoxime**, $C_{10}H_{14}(N.OH)$, obtained from dextro-rotatory carvol (p. 688) with hydroxylamine. Dextro-nitroso-chloride, on the other hand, yields a *lævo-nitroso-limonene* or *lævo-carvoxime*, which also melts at 72°, and otherwise corresponds perfectly with dextro carvoxime (*Annalen*, 246, 227; *Berichte*, 21, Ref. 624). *Inactive carvoxime* is produced by mixing dextro- and lævo-carvoxime. It melts at 93°, and is identical with nitroso-dipentene (see below).

As limonene combines four affinities quite readily (bromine or a halogen hydride) it must very probably contain two divalent C-unions, and is a normal dihydroparacymene. Its relation to carvol shows the position of the divalent unions, corresponding to the formula,



$C_3H_7.\left\langle\begin{matrix}CH - CH_2\\ CH = CH\end{matrix}\right\rangle CH.CH_3$

(Goldschmidt, *Berichte*, 18, 1733).

Dextro- and lævo-limonene-nitroso chlorides can, by crystallization from chloroform, be resolved into two isomeric compounds, $C_{10}H_{16}.NOCl$ (α and β), which would further complicate the relations previously expressed (*Berichte*, 22, Ref. 583).

Dipentene, Cinene, $C_{10}H_{16}$, inactive *Limonene*, is the most stable of the preceding terpenes, and is produced by heating pinene, camphene and limonene to 250–300° (from pinene also by the action of alcoholic sulphuric acid); it is, therefore, present in the Russian and Swedish turpentine oil, obtained by application of great heat (p. 1000). It is associated with cineol in Oleum cinæ, and is derived from terpine hydrate, terpineol and cineol by the withdrawal of water, and further by the distillation of caoutchouc, and the polymerization of the **isoprene**, C_5H_8, formed simultaneously. It may be prepared pure by heating its hydrochloride with aniline or sodium acetate in glacial acetic acid solution. It results upon mixing dextro- and lævo-limonene, and is, therefore, *inactive limonene*. It is a liquid, with an agreeable lemon-like odor.

Its sp. gr. is 0.853. It is optically inactive and boils at 175–176°. Although very stable, it can yet be changed into the isomeric terpinene by alcoholic sulphuric acid, or hydrochloric acid.

Dipentene combines with two molecules of bromine or halogen hydride, forming compounds that differ from those of the two limonenes, and hence it is regarded as a peculiar isomeride. However, the same inactive compounds are also formed by mixing the corresponding derivatives of dextro and laevo-limonene. Nevertheless, these synthetic derivatives (unlike the inactive racemic acid) have the same molecular weights (in solution) as the active limonene compounds (*Annalen*, 246, 231).

Dipentene Tetrabromide, $C_{10}H_{16}Br_4$ (see above), melts at 124–125°. Its crystals are entirely different from those of limonene tetrabromide (melting at 104°). *Dipentene Dihydrochloride*, $C_{10}H_{18}Cl_2$, from limonene, dipentene and moist pinene, consists of rhombic plates, melting at 50°. The *dihydrobromide*, $C_{10}H_{18}Br_2$, formed from terpine and cineol with hydrobromic acid, melts at 64°; the *dihydroiodide*, $C_{10}H_{18}I_2$, consists of rhombic prisms, melting at 77°, or plates that fuse at 79°. *Dipentene-nitroso-chloride*, $C_{10}H_{18}(NO)Cl$, from dipentene by means of amyl nitrite and hydrochloric acid, melts at 102°, is inactive and when digested with alcoholic potash yields inactive *Nitroso-dipentene*, $C_{10}H_{15}(NO)$, melting at 93°. It is identical with the inactive *carvoxime* prepared from dextro-carvoxime and lævo-carvoxime.

(2) **Terpinolene**, $C_{10}H_{15}$, is produced when terpine hydrate, terpineol and cineol are boiled with dilute sulphuric acid, and by heating pinene with the concentrated acid. It boils at 185–190°. The *tetrabromide*, $C_{10}H_{16}Br_4$, is a solid melting at 116°. It combines with two molecules of the halogen hydrides to form compounds, that are probably identical with those of dipentene.

(3) **Sylvestrene**, $C_{10}H_{16}$, occurs in Swedish and Russian turpentine oil. It may be obtained pure by digesting its hydrochloride with aniline, or by boiling it with glacial acetic acid and sodium acetate. It boils at 175 178°, and is optically dextro-rotatory; this also is the case with its compounds. Sulphuric acid imparts an intense blue color to its solutions in anhydrous acetic acid (or in acetic anhydride). Its compounds with two molecules of bromine or the haloid acids are different from those of all other terpenes. The *tetrabromide*, $C_{10}H_{16}Br_4$, melts at 135°. The *dihydrochloride*, $C_{10}H_{16}Cl_2$, melts at 72°, the *dihydrobromide*, $C_{10}H_{18}Br_2$, also at 72°, and the *dihydroiodide*, $C_{10}H_{18}I_2$, at 67°. The *nitroso-chloride*, $C_{10}H_{16}(NO)Cl$, melts at 107°.

(3) Terpinenes and Phellandrene.

These do not unite either with bromine or the haloid acids; consequently, they probably do not have divalent unions in the benzene nucleus. However, like amylene, they form nitrosites with N_2O_3, and are probably unsaturated in the side-chain (*Annalen*, 239, 54; *Berichte*, 21, 175).

Terpinene, $C_{10}H_{16}$, results from a rearrangement of pinene, when the latter is shaken with a little concentrated sulphuric acid, and by boiling dipentene, terpine, phellandrene and cineol with dilute sulphuric acid (*Annalen*, 239, 35). It occurs already formed in cardamon oil. It is very similar to dipentene, boils about 180°, but forms liquid products with the haloid acids. It is the most stable of all the terpenes, and is not changed into any other terpene. Nitrous acid converts it into **Terpinene Nitrosite**, $C_{10}H_{16}(NO)O.NO$, melting at 155°, and yielding nitrolamines with bases (*Berichte*, 22, Ref. 585).

Dextrophellandrene, $C_{10}H_{16}$, occurs in the oil of water fennel (Phellandrium aquaticum), etc. **Lævo-phellandrene** is present in eucalyptus oil. Both boil about 170°, and differ merely in opposite rotatory power. Both become solid and crystalline when shaken with sodium nitrite and acetic acid. They are then *nitrosites*, both of which melt at 103°. In this treatment dextro-phellandrene yields *lævo-nitrosite*, and lævo-phellandrene, *dextro-nitrosite*. By mixing the two nitrosites *inactive nitrosite* is formed; this fully agrees with the active nitrosites (*Annalen*, 246, 232, 265; *Berichte*, 21, Ref. 624).

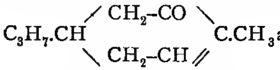
For the terpenes contained in the various ethereal oils see *Berichte*, 22, Ref. 582.

Homologous terpenes have been prepared by the action of sodium upon a mixture of camphor chloride, $C_{10}H_{16}Cl_2$ (p. 1005), and the alkyl iodides. **Ethyl Camphene**, $C_{10}H_{15}(C_2H_5)$, is a liquid with an odor resembling that of oil of turpentine, and boiling at 198–200°. **Isobutyl Camphene**, $C_{10}H_{15}(C_4H_9)$, boils at 228°.

Sesquiterpenes are widely distributed in the ethereal oils. The sesquiterpene in oil of cubeba, patchouly oil, galbanum oil and sabine oil, boils at 274–275°. It forms a *dihydrochloride*, $C_{15}H_{24}.2HCl$, melting at 118°. It can be regenerated from this compound by boiling with aniline (*Annalen*, 238, 78; *Berichte*, 21, 163). **Colophene** is a *diterpene*, $C_{20}H_{32}$, obtained by distilling colophony. It boils at 318°.

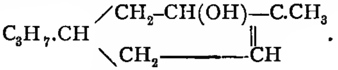
CAMPHOR.

The camphors are peculiar-smelling substances, containing oxygen and intimately related to the terpenes. They are often found with the latter in plant secretions, and can be artificially prepared (in slight quantities) by oxidizing the same. They are derivatives of paracymene, $C_{10}H_{14}$, and mostly derivatives of its tetrahydride $C_{10}H_8$. Japan camphor, $C_{10}H_{16}O$, is a keto-derivative of Borneo camphor, $C_{10}H_{18}O$, a hydroxyl compound of tetrahydro-cymene, corresponding to the following formulas:—



Japan Camphor

and



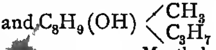
Borneo Camphor.

The ortho-position of the oxygen atom with reference to the methyl group is evident from the ready conversion of Japan camphor into carvacrol or oxycymene (p. 688), and from its analogies to carvol, a keto-derivative of a dihydrocymene (p. 688). Menthol $C_{10}H_{20}O$, bears the same relation to menthone, $C_{10}H_{18}O$ (p. 1007) as Borneo camphor to Japan camphor; the one is an oxy-derivative and the other a keto-derivative of hexahydrocymene, $C_{10}H_{14}(H)_6$:—

$$C_6H_8O\left\langle\begin{matrix}CH_3\\C_3H_7\end{matrix}\right.$$

Menthone.

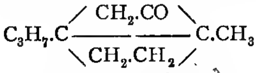
and



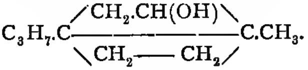
$$C_3H_9(OH)\left\langle\begin{matrix}CH_3\\C_3H_7\end{matrix}\right.$$

Menthol.

As Japan and Borneo camphor are not capable of forming additive products (with bromine or haloid acids), it would appear that a double ethylene union is not present in them; their molecular refraction would also indicate it. To explain this behavior it may be assumed, as in the case of camphene, that the benzene neucleus contains a para-linkage (Brühl, *Berichte*, 21, 467; Wallach, *Annalen*, 230, 269) corresponding to the formulas:—



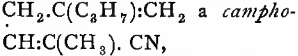
Japan Camphor.



Borneol.

Common or Japan camphor is found in the camphor tree (*Laurus camphora*) indigenous to Japan and China. It is obtained by distillation with steam and sublimation. It is prepared artificially by oxidizing borneol with nitric acid and camphene with chromic acid. It is a colorless, transparent mass, crystallizes from alcohol, and sublimes in shining prisms, of sp. gr. 0.985. It volatilizes at ordinary temperatures, melts at 175°, and distils at 204°. Its alcoholic solution is dextro-rotatory. Camphor yields pure cymene (p. 577), if distilled with P_2O_5, and on boiling with iodine forms carvacrol $C_{10}H_{14}O$ (p. 688). When boiled with nitric acid it yields different acids, chiefly camphoric and camphoronic acids. The

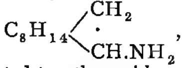
Camphoroxime, $C_{10}H_{16}(N.OH)$, obtained with hydroxylamine, melts at 115° (*Berichte*, **22**, 605) and distils about 250°.

It unites likewise with phenylhydrazine to the *hydrazide* $C_{10}H_{16}(N_2H.C_6H_5)$. *Camphoroxime Anhydride*, $C_{10}H_{15}N$, results from the action of acetyl chloride upon camphoroxime, or of hydrogen chloride upon phenylhydrazide. It boils at 217°. It is probably a cyanide with open chain,  $\begin{array}{l}CH_2.C(C_3H_7):CH_2 \\ \quad\cdot \\ CH:C(CH_3).\,CN,\end{array}$ a *campholene nitrile.* The saponification of the nitrile yields *campholenic acid*, $C_9H_{15}CO_2H$ (Goldschmidt, *Berichte*, **20**, 485; **21**, 1129).

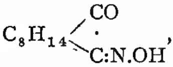
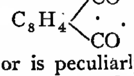
Chlorine and bromine acting upon camphor, produce mono- and disubstitution products.

PCl_5 converts camphor into two **Camphor-dichlorides**, $C_{10}H_{16}Cl_2$ melting at 70° and 155°.

Two *Chlornitrocamphors*, $C_{10}H_{14}Cl(NO_2)O$ (α and β), are produced when chlorcamphor is digested with nitric acid; the copper zinc couple reduces them to α- and *β-nitrocamphor*, $C_{10}H_{15}(NO_2)O$ (*Berichte*, **22**, Ref. 266; **23**, Ref. 115).

Bornylamine, $C_{10}H_{17}.NH_2$ =  $C_8H_{14}\left\langle\begin{array}{l}CH_2 \\ \cdot \\ CH.NH_2\end{array}\right.$, a solid base, melting at 160°, is formed when camphor is heated together with ammonium formate to 240° (*Berichte*, **20**, 104, 483). Bornylamine shows in all respects the character of an alicyclic amine (p. 912). Its odor resembles that of piperidine. It is strongly alkaline, absorbs carbon dioxide from the air, yields a diazoamido-derivative (not an azo-dye) with diazobenzene chloride, and forms a nitrite with nitrous acid (*Berichte*, **21**, 1128).

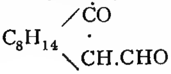
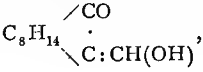
Camphylamine, $C_{10}H_{17}.NH_2 = C_5H_5(C_3H_7)(CH_3).CH_2.NH_2$, is isomeric with the preceding compound. It is formed when sodium and alcohol act upon camphoroxime. It is very probable that the benzene chain present in it is open. It is a liquid boiling at 195°. Its properties resemble those of the amines of the paraffin series (*Berichte*, **20**, 485; **21**, 1128).

Isonitroso-camphor, $C_{10}H_{14}O(N.OH)$ =  $C_8H_{14}\left\langle\begin{array}{l}CO \\ \cdot \\ C:N.OH\end{array}\right.$, is obtained by the action of amyl nitrite and sodium ethylate upon camphor. A CH_2-group is replaced. The compound melts at 153°. Nitrous acid, or sodium bisulphite and boiling with dilute sulphuric acid (p. 326), changes it to *camphor-quinone* = $C_{10}H_{14}O_2$ =  $C_8H_4\left\langle\begin{array}{l}CO \\ \cdot \\ CO\end{array}\right.$. The latter resembles quinone and the (1, 2)-diketones. Its odor is peculiarly sweet. It volatilizes with aqueous vapor and sublimes at 60° in golden yellow needles that melt at 198° (Claisen, *Berichte*, **22**, 530).

Sodium Camphor and *Sodium-Borneo-camphor* separate when metallic sodium acts upon the benzene or toluene solution of camphor:—

$$2C_{10}H_{16}O + 2Na = C_{10}H_{15}NaO + C_{10}H_{17}.ONa.$$

Campholic acid, $C_{10}H_{18}O_2$, and borneol, $C_{10}H_{18}O$, are similarly formed when camphor is heated with alcoholic potash. The alkyl iodides convert sodium camphor into *alkyl camphor*. *Ethyl Camphor*, $C_{10}H_{15}(C_2H_5)O$, boils at 230°.

Camphor Aldehyde,  $C_8H_{14}\left\langle\begin{array}{l}CO \\ \cdot \\ CH.CHO\end{array}\right.$ or  $C_8H_{14}\left\langle\begin{array}{l}CO \\ \cdot \\ C:CH(OH)\end{array}\right.$, melts at 77°.

It is formed by the action of sodium or sodium ethylate and formic ester upon camphor (analogous to the formation of the β-ketonaldehydes, p. 323, 730). It is perfectly analogous to the β-ketonaldehydes. It is acid in nature, and dissolves readily in the caustic alkalies (*Berichte*, 22, 533, 3281; 23, Ref. 39).

The camphors, like the turpentine oils, occurring in different plants, manifest some differences. **Matricaria camphor**, $C_{10}H_{16}O$, or *Lævo-camphor*, contained in the oil of *Matricaria Parthenium*, is lævo-rotatory, and when oxidized with nitric acid yields lævo-camphoric acid. **Lævo-camphoroxime**, $C_{10}H_{16}(N.OH)$, also melts at 115°. **Absinthol**, $C_{10}H_{16}O$, from oil of wormwood (from *Artemesia Absinthium*), is liquid, and boils at 195°. **Myristicol**, $C_{10}H_{16}O$, from nutmeg-oil, boils at 235°. **Pinol**, $C_{10}H_{16}O$, a by-product in the preparation of pinene nitroso chloride, is isomeric with camphor. It boils at 183–184°. Potassium permanganate oxidizes it to terebinic acid, $C_7H_{10}O_4$. **Patchouly Camphor**, $C_{15}H_{28}O$, from Patchouly oil, is a sesqui-camphor. It melts at 55° and boils at 246°. **Caryophyllin**, $C_{20}H_{32}O_2$, is a polymeric camphor, contained in cloves, and melts above 300°.

Borneol, Borneo Camphor, $C_{10}H_{18}O = C_{10}H_{17}.OH$, occurs in *Dryobalanops Camphora*, a tree growing in Borneo and Sumatra. It is artificially prepared by acting with sodium upon the alcoholic solution of common camphor, and bears the same relation to the latter as an alcohol to a ketone. It is quite like Japan camphor, and has a peculiar odor resembling that of peppermint. It sublimes in six-sided leaflets, melts at 198°, and boils at 212°.

Nitric acid oxidizes borneol to common camphor, and then to camphoric acid. Borneol possesses the character of an alicyclic alcohol (of *ac*-tetrahydro-β-naphthol, p. 916) (*Berichte*, 23, 201). It forms esters with organic acids, xanthogenates with CS_2 (*Berichte*, 23, 213), and is especially inclined to form camphene, $C_{10}H_{16}$, by the elimination of water. The acetyl ester, $C_{10}H_{17}.O.C_2H_3O$, boils at 221°. **Bornyl Chloride**, $C_{10}H_{17}Cl$, melting at 148°, is produced by means of PCl_5. It forms borneo camphene by the elimination of HCl.

Lævo-borneol, $C_{10}H_{17}.OH$, is optically opposed to ordinary dextro-borneol. It is produced, together with the latter, when sodium acts upon ordinary camphor.

Cineol and Terpineol are isomerides of borneol.

Cineol, $C_{10}H_{18}O$, is the chief ingredient of worm-seed oil (Artemisia cinæ), cajeput oil and eucalyptus oil. It boils at 176°. Its specific gravity at 16° is 0.923. It forms an unstable hydrochloride additive product, which water resolves into its components. Hydrochloric acid gas conducted into heated cineol produces dipentene-dihydro-chloride, $C_{10}H_{16}.2HCl$ (p. 1002); hydriodic acid gas forms the dipentene-dihydro-iodide, $C_{10}H_{16}.2HI$ (melting at 78°). P_2S_5 converts cineol into cymene. See *Berichte*, 21, 460, 23, Ref. 642, upon the constitution of cineol. Potassium permanganate oxidizes cineol to cineolic acid, $C_{10}H_{16}O_5$, melting at 197° (*Berichte*, 21, Ref. 625; 23, Ref. 641).

Terpineol, $C_{10}H_{18}O$, formed by boiling terpine and terpine hydrate (p. 1000) with aqueous mineral acids, is a thick liquid with a peculiar odor. It boils at 215–218°. It is also produced when pinene stands in contact with alcoholic sulphuric acid; by further absorption of water it yields terpine hydrate. See *Berichte*, 21, 463, in regard to its constitution.

Menthol, Mentha Camphor, $C_{10}H_{20}O = C_{10}H_{19}.OH$, oxyhexahydrocymene (p. 1004), is the chief component of peppermint oil (from Mentha piperita), from which it separates in crystalline form on cooling. It possesses, like borneol, the character of an alicyclic alcohol. It melts at 42°, boils at 213°, and is lævo-rotatory. It forms *esters* with acids and readily parts with water. With concentrated hydrochloric acid, or PCl_5, it yields liquid *menthol chloride*, $C_{10}H_{19}Cl$, boiling at 264°.

Menthene, $C_{10}H_{18}$, is produced when the chloride is acted upon by alkalies, or when menthol is distilled with P_2O_5. It boils at 167°. Chromic acid oxidizes menthol to *dextro-* and *lævo-menthone*, $C_{10}H_{18}O$, which sustain the same relation to menthol that ordinary camphor bears to borneol. The menthones are liquids with an odor resembling that of peppermint. They boil at 206°. They form oximes with hydroxylamine. *Dextro-menthone Oxime*, $C_{10}H_{18}(N.OH)$, is liquid. *Lævo-menthone Oxime* melts at 58°. Acids cause the menthones to change readily from one modification to the other (*Berichte*, 22, Ref. 261). Their activity is due to the asymmetry of a carbon atom (*Annalen*, 250, 362).

The oxidation of the camphors produces different acids, whose constitution has not yet been explained.

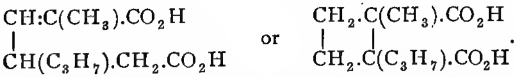
Campholic Acid, $C_{10}H_{18}O_2$, is produced on distilling camphor over heated soda-lime, or with alcoholic potash. It melts at 95° and volatilizes with steam. Nitric acid oxidizes it to camphoric and camphoronic acids.

Camphoric Acid, $C_{10}H_{16}O_4 = C_8H_{14}(CO_2H)_2$, is obtained by boiling camphor with nitric acid (*Annalen*, 163, 323). It crystallizes from hot water in colorless leaflets, melts at 178°, and decomposes into water and its *anhydride*, $C_8H_{14}(CO)_2O$; the latter sublimes readily in shining needles, melts at 217°, and boils at 270°.

The acid from common camphor is dextro-rotatory, that from Matricaria camphor is, however, lævo-rotatory and melts at 197°. The inactive *meso-camphoric acid* is produced on mixing the two acids. It melts at 113°, and is derived from ordinary camphoric acid by heating the latter with hydrochloric acid to 140°.

By the fusion of camphoric acid with potash we get isopropyl succinic acid, $C_2H_3(C_3H_7)(CO_2H)_2$.

From its constitution camphoric acid may be considered either as an unsaturated methylpropyl adipic acid, $C_6H_6(CH_3)(C_3H_7)O_4$ (*Annalen*, 220, 278), or, inasmuch as it cannot form additive compounds, it may be regarded as methyl-propyl tetramethylene dicarboxylic acid, in accordance with the formulas:—



$$\begin{array}{l} CH{:}C(CH_3).CO_2H \\ | \\ CH(C_3H_7).CH_2.CO_2H \end{array} \quad \text{or} \quad \begin{array}{l} CH_2.C(CH_3).CO_2H \\ |\qquad | \\ CH_2.C(C_3H_7).CO_2H \end{array}.$$

Camphoronic Acid, $C_9H_{12}O_5 + H_2O$, is produced by the further oxidation of camphoric acid; it occurs in the mother liquor. It loses its water of crystallization at 100–120°, and melts at 135°. It is tribasic, yields isobutyric acid when fused with potash, and appears to be an isopropyl tricarballylic acid (*Berichte*, Ref. 71 and 18, 328).

RESINS.

The resins are closely related to the terpenes, and occur with them in plants, and are also produced by their oxidation in the air. Their natural, thick solutions in the essential oils and turpentines are called *balsams*, whereas the real *gum resins* are amorphous, mostly vitreous bodies. Their solutions in alcohol, ether or turpentine oils constitute the commercial *varnishes*.

Most natural resins appear to consist of a mixture of different, peculiar acids, the resin acids. The alkalies dissolve them, forming *resin soaps*, from which acids again precipitate the *resin acids*. By their fusion with alkalies we obtain different benzene derivatives (resorcinol, phloroglucin, proto-catechuic acid); and when they are distilled with zinc dust they yield benzenes, naphthalenes, etc.

Colophony is found in turpentine (p. 999), and, in the distillation of the latter, remains as a fused mass. It consists principally of **Abietic Acid**, $C_{44}H_{64}O_5$ (Sylvic acid), which can be extracted by hot alcohol, crystallizes in leaflets, and melts at 139° (147°). When oxidized it yields trimellitic, isophthalic and terebinic acids.

Gallipot Resin, from *Pinus maritima*, contains **pimaric acid**, $C_{20}H_{30}O_2$, which is very similar to sylvic acid and passes into the latter when distilled in vacuo. It melts at 210°. The latest investigations show that pimaric acid consists of three isomerides (*Berichte*, 19, 2167).

Gum lac, obtained from East India fig trees, constitutes what is known as shellac when fused. This is employed in the preparation of sealing wax and varnishes.

Amber is a fossil resin, found in peat-bogs. It consists of succinic acid, two resin acids and a volatile oil. After fusion it dissolves easily in alcohol and turpentine oil, and serves for the preparation of varnishes.

To the *gum resins*, occurring mixed with vegetable gums, and gum in the juice of plants, belong gamboge, euphorbium, asafœtida, caoutchouc and gutta percha.

GLUCOSIDES.

These substances occur in plants and split into sugars (mostly grape sugar), and other bodies (alcohols, aldehydes, phenols), when acted on by acids or ferments. Therefore they are assumed to be ethereal derivatives of the glucoses. Various members of this series, obtainable also by synthesis, have already received notice in connection with the products they yield when they are decomposed. The following have not been fully investigated:—

Æsculin, $C_{15}H_{16}O_9$, is contained in the bark of the horse chestnut; it crystallizes in fine needles with 1½ molecules H_2O, melts when anhydrous at 205°, and is decomposed by acids or ferments into glucoses and æsculetin, $C_9H_6O_4$ (Dioxycoumarin, p. 822). **Daphnin**, $C_{15}H_{16}O_9 + 2H_2O$, is isomeric with æsculin, and is obtained from the bark of *Daphne alpina.* It melts at 200°, and breaks down into glucose and daphnetin (Dioxycoumarin, p. 823).

Arbutin, $C_{12}H_{16}O_7$, and **Methyl Arbutin**, $C_{13}H_{18}O_7$, are found in the leaves of *Arbutus uva ursi.* By their decomposition, we get, besides grape sugar, hydroquinone or methyl hydroquinone. Arbutin crystallizes in fine needles, with ½–1 molecule of water, melts at 187° (*Berichte*, 16, 1925) in the anhydrous state, and is colored a deep blue by ferric chloride. *Methyl Arbutin* contains 1 molecule of water, and melts at 176°. It is formed artificially from arbutin by the action of methyl iodide and potash.

Hesperidin, $C_{22}H_{26}O_{12}$, is present in the unripe fruit of oranges, lemons, etc. It separates from alcohol in fine needles, melts at 251°, and is decomposed into grape sugar and **Hesperitin**, $C_{16}H_{14}O_6$, which by further boiling with potassium hydroxide breaks up into hesperitinic acid (isoferulic acid, p. 821), and phloroglucin, $C_6H_3.(OH)_3$.

Phloridzin, $C_{21}H_{24}O_{10}$, occurs in the root bark of various fruit trees, crystallizes with $2H_2O$ in fine prisms, and when anhydrous melts at 108°. By decomposition it yields grape sugar and **Phloretin**, $C_{15}H_{14}O_{15}$ (colorless leaflets), which alkalies convert into phloretic acid (p. 775), and phloroglucin.

Quercitrin, $C_{36}H_{36}O_{20}$, is found in the bark of *Quercus tinctoria*, and is applied as a yellow dye under the name *Quercitrone.* It consists of yellow needles or leaflets, which are decomposed into isodulcitol and **Quercitin**, $C_{24}H_{16}O_{11} + 3H_2O$. The latter forms an *hexa-ethyl* and *octo-acetyl* derivative (*Berichte*, 17, 1680). Fused with alkalies it yields quercitinic acid, $C_{15}H_{10}O_7$, protocatechuic acid and phloroglucin.

Saponin, $C_{32}H_{54}O_{18}$, in the roots of Saponaria officinalis, is a white amorphous powder, provoking sneezing, and in aqueous solution forms a strong lather. Its decomposition products are glucose and sapogenin, $C_{14}H_{22}O_2$.

Glucosides whose decomposition products belong to the fatty series are:—

Convolvulin, $C_{31}H_{50}O_{16}$, derived from the roots of Jalap (from *Convolvulus purga*). It is a gummy mass, and is a strong purgative. It dissolves in alkalies to **Convolvulic Acid**, $C_{31}H_{52}O_{17}$ (?), which nitric acid converts into **Ipomic Acid**, $C_{10}H_{18}O_4 = C_8H_{16}(CO_2H)_2$.

Jalapin, $C_{34}H_{56}O_{16}$, from *Convolvulus orizabensis*, is very similar to convolvulin, and forms analogous derivatives.

Myronic Acid, $C_{10}H_{19}NS_2O_{10}$, occurs as potassium salt in the seeds of black mustard. This crystallizes from water in bright needles. On boiling it with baryta water, or by the action of the ferment *myrosin*, present in the seed, the salt decomposes into glucose, allyl mustard oil, and primary potassium sulphate:—

$$C_{10}H_{18}KNS_2O_{10} = C_6H_{12}O_6 + C_3H_5.N{:}CS + SO_4KH.$$

BITTER PRINCIPLES.

Under the head of "bitter principles," or indifferent substances, is embraced a class of vegetable bodies whose chemical character is but indistinctly indicated. Many of them have already found their place in the chemical system. Those yet uninvestigated are:—

Aloïn, $C_{17}H_{18}O_7$, found in aloes, the dried sap of many plants of the aloe variety. It forms fine needles, possesses a very bitter taste, and acts as a strong purgative. If digested with nitric acid it yields *aloetic acid*, $C_{14}H_4(NO_2)_4O_2$, and chrysammic acid (p. 900). It forms *alorcinic acid*, $C_9H_{10}O_3 + H_2O$, when fused with caustic potash. This breaks down into orcin and acetic acid.

Cantharidin, $C_{10}H_{12}O_4$, contained in Spanish flies and other insects, crystallizes in prisms or leaflets, melts at 218°, and sublimes readily. It tastes very bitter and produces blisters on the skin. It dissolves when heated with alkalies and forms salts of *cantharinic acid*, $C_{10}H_{14}O_5 = C_8H_{13}O_2.CO.CO_2H$. Hydriodic acid converts cantharidin into *cantharic acid*, $C_{10}H_{12}O_4 = C_8H_{11}O.CO.CO_2H$, isomeric with it.

Picrotoxin, $C_{15}H_{16}O_6 + H_2O$, is found in the grains of cockle, and crystallizes in fine needles, melting at 201°. It has an extremely bitter taste and is very poisonous.

Santonin, $C_{15}H_{18}O_3$, is the active principle of worm-seed, crystallizes in shining prisms, and melts at 170°. It dissolves in alkalies to salts of **Santonic Acid**, $C_{15}H_{20}O_4$, which breaks down at 120° into water and santonin. On boiling with baryta water we have formed salts of isomeric **santoic acid**, $C_{15}H_{20}O_4$, which melts at 171°. Santonin, therefore, bears the same relation to these two acids as coumarin to coumarinic and coumaric acids. When santonin is boiled with hydriodic acid *a*- and *β-meta santonin*, *santonid* and *para santonid* (Cannizaro, *Berichte*, 18, 2746; 22, Ref. 732),—compounds isomeric with santonin—are produced.

The following are unstudied coloring matters; some of them appear to have a constitution analogous to the phthaleïns (p. 881):—

Brasilin, $C_{16}H_{14}O_5$, is found in Brazil-wood and red wood; crystallizes in white, shining needles, and dissolves in alkalies with a carmine-red color on exposure to the air. Acids then precipitate *brasilin*, $C_{16}H_{12}O_5 + H_2O$, from the solution. The action of iodine upon brasileïn also produces this compound. It regenerates brasilin by reduction. When distilled it yields resorcinol (*Berichte*, 23, 1428).

Carthamin, $C_{14}H_{16}O_7$, occurs in safflower, the blossoms of *Carthamus tinctorium*, and is precipitated from its soda solution by acetic acid, as a dark red powder, which, on drying, acquires a metallic lustre. It dissolves with a beautiful red color in alcohol and the alkalies. It yields para-oxybenzoic acid with caustic potash.

Curcumin, $C_{14}H_{14}O_4$, the coloring matter of turmeric, crystallizes in orange-yellow prisms, melts at 177°, and dissolves in the alkalies to brownish-red salts. Ethyl vanillic acid is obtained on oxidizing diethyl-curcumin with potassium permanganate.

Euxanthinic Acid, $C_{19}H_{18}O_{11}$ (Porrisic acid), occurs as magnesium salt in so-called purrée (jaune indien), a yellow coloring matter from India and China, (*Annalen*, 254, 265). It crystallizes from alcohol in yellow prisms with one molecule of water. When boiled with dilute sulphuric acid it splits up into glycuronic acid and **euxanthone**, $C_{13}H_8O_4$ (p. 860).

Hæmatoxylin, $C_{16}H_{14}O_6$, the coloring matter of logwood (Hæmatoxylon Campechianum), is very soluble in water and alcohol, and crystallizes in yellowish prisms with $3H_2O$. It dissolves in alkalies with a violet-blue color. When distilled or fused with potassium hydroxide, pyrogallic acid and resorcinol result from it. If the ammonium hydroxide solution be allowed to stand exposed to the air there results **hæmateïn-ammonia**, $C_{16}H_{11}(NH_4)O_6$, from which acetic acid liberates **Hæmateïn**, $C_{16}H_{12}O_6$, a red-brown powder with metallic lustre, when dried.

Gentisin, $C_{14}H_{10}O_5$, contained in the Gentian root, crystallizes in yellow needles, and fused with caustic potash yields hydroquinone carboxylic acid (p. 778) and phloroglucin.

Carminic Acid, $C_{17}H_{18}O_{10}$, occurs in the buds of certain plants, and especially in cochineal, an insect inhabiting different varieties of cactus. It is an amorphous purple-red mass, very readily soluble in water and alcohol, and yields red salts with the alkalies. When boiled with dilute sulphuric acid it splits into a non-fermentable sugar and **carmine-red**, $C_{11}H_{12}O_7$. When distilled with zinc dust it yields the hydrocarbon, $C_{16}H_{12}$. On boiling carminic acid with nitric acid we get **nitrococcic acid**.

Chlorophyll occurs in the chlorophyll granules in all the green parts of plants. Wax and other substances are associated with it. We do not yet know its constitution. There seems to be an essential quantity of iron in it.

The following are *animal substances* the more extended discussion of which belongs to the province of physiological chemistry.

BILIARY SUBSTANCES.

In the bile, the liquid secretion of the liver, essential to the digestion of fats, occur (in addition to fats, mucous substances and albuminoids) the sodium salts of two peculiar acids, **glycocholic** and **taurocholic**; also **cholesterine** and **bile pigments** (bilirubin, biliverdin).

Cholesterine, $C_{26}H_{44}O(C_{27}H_{46}O)$ (*Berichte*, 21, Ref. 657), occurs in not only the bile, but in the blood, in the brain, and in the yolk of eggs, also in the seed and sprouts of many plants, in which it is often confounded with the fats. It is soluble in alcohol and ether, crystallizes in mother-of-pearl leaflets, containing $1H_2O$, and possessing a fatty feel. It parts with its water of crystallization at 100°, melts at 145°, and distils at 360° with scarcely any decomposition. If sulphuric acid be added to the chloroform solution of cholesterine, the chloroform acquires a purple-red color, and on evaporation assumes a blue, then green, and finally a violet coloration. Chemically cholesterine behaves like a monovalent alcohol, and forms esters with acids.

Isocholesterine, $C_{26}H_{44}O$, an isomeric body, occurs associated with cholesterine in distilled sheeps' fat, melts at 138°, and does not give any color reactions with chloroform and sulphuric acid. **Phytosterine**, present in plant seeds and sprouts, is very similar to cholesterine, and is frequently confounded with the fats.

Lanoline, obtained from raw sheeps' wool, contains esters of cholesterine and isocholesterine with the higher fatty acids. It is applied as a salve, as it will take up water and is absorbed by the skin.

Glycocholic Acid, $C_{23}H_{43}NO_6$, separated in crystalline form from its sodium salt (found in bile) by dilute sulphuric acid, is sparingly soluble in water. It crystallizes in minute needles, melting at 133°. On adding a sugar solution and concentrated sulphuric acid or phosphoric acid to glycocholic acid we obtain a purple-red color. Boiled with alkalies it decomposes into glycocoll and cholic acid.

Taurocholic Acid, $C_{24}H_{45}NOS_7$, is very soluble in water and alcohol, crystallizes in fine needles, and when boiled with water breaks up into cholic acid and taurine. For the separation of glycocholic acid and taurocholic acid from bile see *Journ. pract. Chem.*, 19, 305.

Cholic Acid, Cholalic Acid, $C_{24}H_{42}O_5$ (*Berichte*, 19, 2009; 20, 1968) or $C_{25}H_{42}O_5$ (*Berichte*, 20, 1052), from glyco- and taurocholic acids, crystallizes from hot water in small anhydrous prisms, which dissolve with difficulty in water, and when anhydrous melt at 195°. It reacts the same as glycocholic acid with sugar and sulphuric acid. It is monobasic; its esters are crystalline. It forms a blue compound with iodine, quite similar to that given by starch and iodine (*Berichte*, 20, 683).

GELATINOUS TISSUES AND GELATINES.

These are mostly nitrogenous, organized substances, which on boiling with water are converted into gelatines and are distinguished as *collagenes* and *chondrogenes*. The former constitute bone cartilage and sinews, the connective tissues, the skin and fish-bladder, and afford the ordinary true gelatines; the latter contained in the unhardened cartilage, yield chondrin. As regards composition, both are very similar to the albuminoids, but differ from the latter, mainly in that they are not precipitated by nitric acid and potassium ferrocyanide.

Glutin, gelatine, is precipitated from its aqueous solution by alcohol, and when pure is a colorless, solid mass, without odor and taste. In cold water it swells up, and on boiling dissolves to a thin solution, which gelatinizes on cooling. By the addition of concentrated acetic acid or protracted boiling with a little nitric acid, the solution loses the property of gelatinizing (liquid gelatin). Tannic acid precipitates from the aqueous solution gelatine tannate, a yellowish, glutinous precipitate. The substances yielding gelatine combine also with tannic acid, withdrawing the latter completely from its solutions and forming leather.

Glycocoll and leucine are the principal substances produced on boiling gelatine with sulphuric acid or alkalies. Dry distillation produces bases of the fatty and pyridine series.

Alcoholic hydrochloric acid changes gelatine into a compound that nitrous acid converts into a substance, $C_5H_6N_2O_3$, very similar to the diazo fatty-acids. It may be that it represents **diazo-oxyacrylic ester**, $CN_2{:}C(OH).CO_2.C_2H_5$ (*Berichte*, 19, 850).

Chondrin, from bone cartilage, is very similar to the preceding, and is distinguished from it by the fact that it is precipitated from its aqueous solution by alum, lead acetate, and most metallic salts; on the other hand, it is not precipitated by mercuric chloride, whereas it is otherwise with glutin. It affords leucine and not glycocoll if boiled with dilute sulphuric acid. **Chitine** belongs to the class of substances present in bone cartilage. It is the chief component of the shells of crabs, lobsters, etc. Boiling acids convert it into glucosamine, $C_6H_{13}NO_5$ (p. 505).

ALBUMINOID SUBSTANCES, ALBUMINATES.

These were formerly known as proteïn substances, and form the principal constituents of the animal organism. They also occur in plants (chiefly in the seeds), in which they are produced exclusively. When absorbed into the animal organism as nutritive matter they sustain but very slight alteration in the process of assimilation.

They exhibit great conformity in their properties and especially in their composition, as seen from the following percentage numbers of the three most important varieties of albumen :—

	Albumen.	Fibrin.	Caseïn.
C	53.5 per cent.	52.7 per cent.	53.8 per cent.
H	7.0 " "	6.9 " "	7.2 " "
N	15.5 " "	15.4 " "	15.6 " "
O	22.4 " "	23.8 " "	22.5 " "
S	1.9 " "	1.2 " "	0.9 " "

Owing to indistinct chemical character and great power of reaction, no accurate molecular formulas have been deduced for the albuminoids up to the present. The formula of Lieberkühn, $C_{72}H_{112}SN_{18}O_{22}$, affords an approximate representation. Loew thinks this should be trebled (*Berichte*, **23**, 43; **22**, 3046).

The decomposition products of the albuminoids give us an idea as to their constitution. These they yield when boiled with dilute sulphuric or hydrochloric acid, or with baryta water.

The decomposition products are mainly amido-acids of the fatty series: glycocoll, leucine, leuceïnes, $C_nH_{2n-1}O_2$ (unsaturated glycines), aspartic and glutaminic acids, $C_5H_9NO_4$ (p. 467), as well as phenylamidopropionic acid, tyrosine, etc. All albuminoids yield the same products, only in relatively different amounts, therefore they must be assumed to form from the union of these constituents (See *Berichte*, **18**, Ref. 444; **19**, Ref. 30, 697).

Putrefaction causes a similar decomposition, but in addition to amido-acids fatty acids and aromatic acids, as well as phenols, indol, skatole and skatole-acetic acid are produced (*Berichte*, 22, Ref. 702). Basic compounds also result in this decomposition. These are the diamines and imines of the paraffin series, and have been called *ptomaines* or *toxines* (p. 316).

Certain pathogenic micro-organisms, as diphtheria and anthrax bacilli, produce a decomposition that is far more extended, and results in the formation of poisonous, substances somewhat similar to albumen and peptone, which have been termed *toxalbumens;* these lose their toxic properties when their aqueous solutions are heated (*Berichte*, 23, Ref. 351).

Tuberculin is a member of this series. It is the active substance that has been extracted by means of aqueous glycerol from tubercular bacilli cultures. The percentage content of its solution is not known, its composition is unknown, its injurious action has never been determined and yet it has, very recently, been suggested as a curative for tuberculosis.

Most albuminoids exist in two modifications, one *soluble* the other *insoluble* in water. Alcohol, ether, tannic acid, many mineral acids and metallic salts reprecipitate them from their aqueous solutions. In their coagulated condition they are dry, white, amorphous masses. Most of them dissolve in dilute mineral acids, all, however, in concentrated acetic acid and in phosphoric acid on application of heat. Ferro- and ferri-cyanide of potassium precipitate them from their dilute acetic acid solution. They dissolve in dilute alkalies, with the separation of sulphur in form of sulphide. The substances reprecipitated by dilute acetic acid are very similar to the albuminoids employed.

Reactions.—All albuminoids are colored a violet red on warming with a mercuric nitrate solution containing a little nitrous acid (this is like tyrosine). On the addition of sugar and concentrated sulphuric acid they acquire a red coloration, which on exposure to the air becomes dark violet. If concentrated sulphuric acid be added to the acetic acid solution of albuminoids they receive a violet coloration and show a characteristic absorption band in the spectrum.

Gastric juice, pepsine and dilute hydrochloric acid, and various other ferments dissolve the albuminoids at 30-40°, converting them first into anti- and hemi albuminoses, which later become so-called *peptones*. These dissolve readily in water, are not coagulated by heat and are not precipitated by most of the reagents (*Berichte*, 16, 1152; 17, Ref. 79).

The manner of distinguishing and classifying the various albuminoids is yet very uncertain. According to the manner in which they pass from the soluble into the insoluble state we distinguish three principal groups of albuminoids; the *albumins*, *fibrins* and *caseïns*. The first are soluble in pure water, coagulate when heated alone or after acidulation with a few drops of nitric acid, and are then no longer soluble in dilute potassium hydroxide or acetic acid. The fibrins coagulate immediately after their exit from the animal organism. The caseïns (legumins) are almost insoluble in water, dissolve, however, very readily in dilute alkalies and alkaline phosphates, and are again precipitated from these solutions on acidulating them.

1. The albumins exist in the following varieties:—

Egg Albumin is obtained by precipitating its aqueous solution with basic lead acetate, decomposing the precipitate with carbon dioxide and hydrogen sulphide and then reducing the filtrate at a temperature below 60°. It is a yellowish, gummy mass, which swells up in water and then dissolves. The perfectly neutral solution coagulates at 72–73°; it is lævo-rotatory and is precipitated by alcohol, by shaking with ether and by dilute acids.

Serum Albumin occurs in the blood, in the lymph and in the various secretions. It is obtained from the blood serum diluted with water (subsequent to the removal of other albuminoids by a little acetic acid) in the same manner as egg albumin. It resembles the latter, but is not precipitated by dilute mineral acids.

Vegetable Albumin occurs in almost all vegetable juices. It coagulates on warming and is very similar to egg fibrin. *Vitellin*, contained dissolved in the yellow of the egg, appears to be a mixture of albumin and caseïn.

2. *Fibrins.*

Blood fibrin separates from the blood after the latter has been discharged from the organism. It seems that it does not exist already formed in the blood, but that it results by the union of the so-called *fibrinoplastic* (contained in the serum) and *fibrinogen* (in the blood corpuscles) *substances.* Fibrin is obtained by whipping the fresh blood, when it separates in long fibres, which are freed from blood corpuscles by long-continued kneading under water. It is a whitish, sticky, fibrinous mass, which becomes hard and brittle upon drying. It is insoluble in water, dilute hydrochloric acid and a solution of common salt.

Myosin constitutes (with water) the chief constituent of the muscles, in which it seems to exist in a dissolved state. It is obtained by dissolving the well washed muscles in a moderately dilute sodium chloride solution and precipitating the filtrate with salt. *Vegetable fibrin* occurs in an undissolved state in the grain granules. On kneading flour (stirred to a paste) under water, the starch granules are washed out, together with the soluble albumin, and there remains a pasty mass called *gluten*, which, according to Ritthausen, consists of *glicidin* (vegetable gelatine), *mucedin* and *gluten fibrin.* The latter is soluble in dilute alcohol and acids. When seeds sprout the vegetable fibrin is converted into the soluble ferment called *diastase* (*Berichte*, 23, Ref. 210). The other unformed ferments (p. 508) appear also to be modified albuminoids.

2. *Caseïns.*

Milk caseïn occurs dissolved in the milk of all mammalia, and on the addition of hydrochloric acid separates as a flocculent precipitate, which is washed out with water, alcohol and ether (for the removal of the fats). Pure caseïn is not soluble in pure water, but in water containing a little hydrochloric acid or alkali. When the solutions are neutralized it is reprecipitated. The solutions do not coagulate until heated to 130–140°. If a few drops of hydrochloric acid or rennet be added to milk all the caseïn will be co-precipitated with the fat globules (cheese); in the solution (whey) remain milk, sugar, lactic acid and salts.

Vegetable Caseïn, or Legumin, occurs chiefly in the seeds of leguminous plants, and is perfectly similar to caseïn. It is precipitated from the pressed out juice by acids or rennet.

In concluding the albuminates mention may be made of the *hæmoglobins* and *lecithin.*

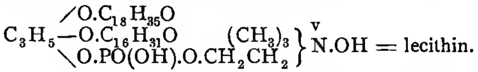
The *oxyhæmoglobins* are found in the arterial blood of animals and may be obtained in crystalline form from the blood corpuscles by treatment with a solution of sodium chloride and ether, and the addition of alcohol. The different oxyhæmoglobins, isolated from the blood of various animals, exhibit some variations, especially in crystalline form. They are bright red, crystalline powders, very soluble in cold water, and are precipitated in crystalline form by alcohol. When the aqueous solution of oxyhæmoglobin is placed under the air pump or through the agency of reducing agents (ammonium sulphide) it parts with oxygen and becomes *hæmoglobin.* The latter is also present in venous blood and may be separated out in a crystalline form (*Berichte*, 19, 128). Its aqueous solution absorbs oyxgen very rapidly from the air, and reverts again to oxyhæmoglobin. Both bodies in aqueous solution exhibit characteristic absorption spectra, whereby they may be easily distinguished.

If carbon monoxide be conducted into the oxy-hæmoglobin solution, oxygen is also displaced and hæmoglobin-carbon monoxide formed. This can be obtained in large crystals with a bluish color. This explains the poisonous action of carbon monoxide. The bluish-red solution of hæmoglobin-carbon monoxide shows two characteristic absorption spectra. These do not disappear upon the addition of ammonium sulphide (distinction from oxy-hæmoglobin).

On heating to 70°, or through the action of acids or alkalies, oxyhæmoglobin is split up into albuminoids, fatty acids and the pigment *hæmatin*, which in a dry condition is a dark brown powder. It contains 9 per cent. iron, and, as it appears, corresponds to the formula, $C_{34}H_{34}FeN_4O_5$.

The addition of a drop of glacial acetic acid and very little salt to oxyhæmoglobin (or dried blood) aided by heat, produces microscopic reddish-brown crystals of hæmin (hæmatin hydrochloride) (*Berichte*, 18, Ref. 232); alkalies separate hæmatin again from it. The production of these crystals serves as a delicate reaction for the detection of blood.

Lecithin, $C_{42}H_{88}NPO_9$ (Protagon), is widely distributed in the animal organism and occurs especially in the brain, in the nerves, the blood corpuscles, and the yellow of egg, from which it is most easily prepared. It is a wax-like mass, easily soluble in alcohol and ether, and crystallizes in fine needles. It swells up in water and forms an opalescent solution, from which it is reprecipitated by various salts. It unites with bases and acids to salts, forming a sparingly soluble double salt, $(C_{42}H_{84}NPO_8.HCl)_2.PtCl_4$, with platinic chloride. Lecithin decomposes into choline, glycerol-phosphoric acid (p. 454), stearic acid and palmitic acid, when it is boiled with acids or baryta water. Therefore we assume it to be an ethereal compound of choline with glycero-phosphoric acid, combined as glyceride with stearic and palmitic acids:—



$$C_3H_5\begin{array}{l}\diagup O.C_{18}H_{35}O\\ -O.C_{16}H_{31}O \qquad (CH_3)_3\\ \diagdown O.PO(OH).O.CH_2CH_2\end{array}\Big\}\overset{v}{N}.OH = \text{lecithin}.$$

INDEX.